CHEMISTRY LIBRARY
May 8'56

JOURNAL

OF THE

INDIAN CHEMICAL SOCIETY

VOL. XXXIII FEBRUARY, 1956 No. 2

CONTENTS

		PAGE
17.	Steroid compounds. Part V. Tricyclic intermediates for the synthesis of D-homosteroid.—By N. K. Chaudhuri and P. C. Mukharji	81
18.	Ion exchange behaviour of resorcinol-formaldehyde resin.—By S. L. Gupta ...	90
19.	Steroid compounds. Part VI. Some experiments towards the synthesis of 11-keto steroids.—By P. C. Mukharji	99
20.	Infra-red studies of sterculic acid and some related compounds.—By J. P. Verma, Sharda Das Gupta, Bhola Nath and J. S. Aggarwal	111
21.	Studies in chromium oxide sols. Part I. Electrical conductivity of chromium oxide sol.—By A. K. M. Trivedi, C. S. Bhatt and A. S. Divatia ...	115
22.	Studies in carbohydrates. Part III. Investigation of Modal gum (*Lannea grandis*).—By V. M. Parikh, T. R. Ingle and B. V. Bhide ...	119
23.	Determination of the solubility product of nickel hydroxide.—By P. K. Jena and B. Prasad	122
24.	Studies in carbohydrates. Part IV. Investigation of Modal gum (*Lannea grandis*). Structure of the aldobionic acid.—By V. M. Parikh, T. R. Ingle and B. V. Bhide	125
25.	Studies in Friedel-Crafts' acylation. Part I. Friedel-Crafts' acetylation of acetanilide and aceto-*o*-toluidide.—By (Miss) M. J. Sacha and S. R. Patel ...	129
26.	Micro-method for estimation of nicotine group of alkaloids in tobacco plants.—By B. C. Bose, H. N. De and I. H. Dalal	131
27.	Pechmann reaction: Coumarins from 2-ethylquinol and 4-ethylpyrogallol.—By D. H. Mehta, R. S. Salimath and N. M. Shah	135
28.	Synthesis of 6-halogenated 2 : 3-disubstituted quinazol-4-ones. Part III.—By R. S. Salimath, S. R. Patel and N. M. Shah	140
29.	Bromination of compounds containing two aromatic nuclei. Part XVI. Bromination of some arylamides of 2-hydroxy-3-methylbenzoic acid (3-cresotic acid).—By Mrs. V. R. Patakoot and G. V. Jadhav	143
30.	On the quantitative estimation of beryllium. Part I. As barium fluoberyllate gravimetrically.—By R. K. Dutta and A. K. Sen Gupta	146
31.	Application of refractive index in the study of chemical constitution. Part I. Determination of transition point of certain hydrated inorganic salts in solution by refractive index.—By Shiam Sunder Joshi and D. P. Joshi ...	149
32.	Possible antituberculous compounds. Part V. Preparation of benzylidene and benzyl derivatives of 4′-acyl-4-aminodiphenyls.—By Vinay S. Misra and Maheshwari P. Khare	153

UNIVERSITY OF ILLINOIS MAY 1 1956

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

READY DELIVERY

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

ANALYTICAL BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTICAL BALANCE

CAPACITY: 200 Gms. SENSITIVITY: $\frac{1}{10}$ Mgm. 5 Divisions throw of pointer for addition of 1 Mgm.

ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

Distributors:

ADAIR, DUTT & Co. (INDIA) Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

QUICKFIT & QUARTZ Ltd.

now introduce

CRAIG

COUNTER-CURRENT LIQUID/LIQUID EXTRACTION MACHINE

Three models offered:

FULLY AUTOMATIC * SEMI-AUTOMATIC * MANUAL

Also available:

'QUICKFIT' GENERAL EQUIPMENT SET ...	... Cat. No. 3 BE
'QUICKFIT' LABORATORY EQUIPMENT SET ...	... Cat. No. 10 BE
'QUICKFIT' GENERAL UTILITY SET ...	... Cat. No. 2 BU
'QUICKFIT' SEMI-MICRO ORGANIC PREPARATION APPARATUS WITH GROUND-IN THERMOMETERS	Cat. No. 3 MU
QUICKFIT' STADLER STILLS FOR PYROGEN-FREE WATER	Cat. No. 35 DWA
'QUICKFIT' DEAN & STARK MOISTURE DETERMINATION APPARATUS	Cat. No. 10 DM

* * * * *

ENDECOTTS FILTERS LTD. ENGLAND

LABORATORY TEST SIEVES AVAILABLE FROM STOCK

1 B.S. SPECIFICATIONS SIEVES
FROM MESH NO. 5 to MESH NO. 300

2 A.S.T.M. STANDARD SIEVES
FROM MESH NO. 4 TO MESH NO. 400

3 'POCKET INTERCHANGER' SIEVES
4" DIAMETER WITH DISCS
FROM MESH NO. 7 TO MESH NO. 200.

*

For details and prices, please write to Accredited Distributors:

UNION SCIENTIFIC SYNDICATE

52-58 BABU GENU ROAD, P.O. BOX No. 2448

BOMBAY 2

Gram: 'PETROLIUM' Phone: 28465

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted in typescript with double line and marginal spacings. Tables and foot-notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm., c.c., ml., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its 'List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "Found:———; ———. ——— requires ——— per cent". Analytical results for compounds which have been previously known should be given in the form: "Found:——; ———. Calc. for———: ———; ———."

12. Every paper should be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

Change of address should be immediately intimated to the office

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue	Rs. 3		
Annual Subscription	,, 20 (for Fellows)	20	28
	,, 24 (for Subscribers)	28	32
	,, 28 (Composite)	34	40

Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page ...	... Rs. 40/-
Half Page ...	... ,, 25/-
Quarter Page ...	... ,, 15/-

In Cover Pages:

Cover (Back) Full ...	Rs. 100/-
,, ,, Half ...	,, 60/-

In special positions:

Page facing first reading matter ...	Rs. 70/-
Page facing last page of reading matter...	,, 60/-

Second and Third Pages:

Full Page ...	Rs. 70/-
Half Page ...	,, 40/-
Quarter Page ...	,, 25/-

Page facing inside front cover ...	,, 50/-
Page facing inside back cover ...	,, 50/

Closing date for advertising materials: 7th of the previous month.
The above rates apply also to the Industrial and News Edition.

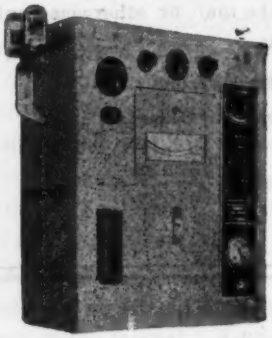
10% *Rebate allowed in cases of six consecutive full and halfpage insertions.*

All communications are to be addressed to:

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road, Calcutta-9.

EX: DR. B. LANGE-GERMANY
FLAME PHOTOMETER
(Model V)

This Flame Photometer is especially useful for rapid determination of Alkali metals for which no other more rapid and easier methods of analysis are known.



Besides these elements more than 30 other elements can also be determined accurately. Special interference filters are available for the elements. It has got a built-in compressor and can be worked on city gas.

A Lithium compensation accessory for overcoming interferences is also available.

Special accessories can be supplied for using the instrument as a precision absorptiometer.

EXCLUSIVE AGENTS

TOSHNIWAL BROTHERS LTD.

198, Jamshedji Tata Road, BOMBAY 1.

Delhi Office :
3/7, Mutiny Memorial Road,
New DELHI 6.

Madras Office :
9, Blackers Road,
MADRAS 2.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

STEROID COMPOUNDS. PART V. TRICYCLIC INTERMEDIATES FOR THE SYNTHESIS OF D-HOMOSTEROIDS *

By N. K. Chaudhuri and P. C. Mukharji

From 1-methyl*cyclo*hexane-2 : 6-dione and the Mannich base from γ-acetobutyric acid, the tricyclic derivatives (IX and X) have been synthesised.

In Part I of this series (Mukharji, this *Journal*, 1947, **24**, 91) the synthesis of the bicyclic keto-ester (II) was described, and this was in one step converted into the tricyclic ketone (III). A simplified synthesis of compounds of the type (II) in proper stereoisomeric form was warranted in order that the method might be of any practical value in steroid synthesis. In the same paper it was indicated that the Mannich base, ethyl 6-diethylamino-4 ketohexan-1-carboxylate, would be a very useful intermediate in this respect.

A programme of research in this direction was therefore undertaken in 1949, and the first objective was achieved by the preparation of the Mannich base, ethyl 6-piperidino-4-ketohexan-1-carboxylate (XV) (Chaudhuri and Mukharji, *ibid.*, 1952, **29**, 336). The attempted condensation of this Mannich base with 2-methyl*cyclo*pentanone in presence of basic catalysts (cf. Du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 1937, 53; McQuillin and Robinson, *ibid.*, 1938 1097) gave disappointing results, whereas with the sodio derivatives of β-keto-esters like *cyclo*pentanone- and *cyclo*hexanone-2-carboxylates, the reaction proceeded very smoothly and the condensation products in each case were obtained in excellent yields (cf. Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469).

We accordingly turned our attention to a study of the reaction of the above Mannich base with 1-methyl*cyclo*hexane-2 : 6-dione (IV : Blaise Maire, *Compt. rend.*, 1907, **144**, 573). Several factors influenced this decision. Firstly, it was more readily accessible than the corresponding *cyclo*pentane analogue, 1-methyl*cyclo*pentane-2 : 5-dione, and being a β-diketone was expected to react in yields comparable with β-keto-esters. Secondly, we argued that since decalin was stable in the *trans* configuration, reduction of the double bond in (VI) in contrast to systems like (I) under suitable conditions would produce at least a mixture of the *cis* and *trans* forms in which the latter might predominate. The reverse ratio of isomers could be expected in the reduction of the system (I) because of the greater stability of *cis*-hydrindane. To establish *trans* locking at this stage was essential for the ultimate success of the scheme.

While the work with 1-methyl*cyclo*hexane-2 : 6-dione was in progress, Wieland *et al.* (*Helv. Chim. Acta*, 1953, **36**, 377) quite independently, and perhaps unaware of our previous publications, published an account of their work which was essentially identical with ours in the general approach and differed only in the detail of execution. A preliminary note of our work had already been published (*Science & Culture*, 1953,

* Abstracted from the thesis submitted by N. K. C. for the D. Phil. degree in Chemistry of the University of Calcutta.

18, 602 ; 1954, **19**, 463). Because the variants employed by us were an improvement over their method and since some of the intermediate compounds had been more fully characterised by us, the publication of this complete report was considered desirable.

In the beginning we tried condensation of the methoiodide of the base (XV) with the sodio derivative of 1-methyl*cyclo*hexane-2 : 6-dione under conditions described by Wilds and Shunk (*J. Amer. Chem. Soc.*, 1949, **71**, 3956). The reaction product was an acid (m.p. 142°) and very little neutral material was formed. Under identical conditions we found that the methoiodide of diethylaminobutanone furnished an acid of m.p. 46-47° almost exclusively. After we had carried out these experiments, Wendler, Slates and Tishler (*ibid.*, 1951, **73**, 3816) published an account of their work and confirmed the structure (XI) for the acid, m.p. 46-47°. Our acid of m.p. 142° ($\lambda_{max}^{alcohol}$, 250 mμ) was found to be dibasic and presumably arose through the same process with concomitant hydrolysis of the primary ester group. No attempts were made to establish the constitution of this acid to which structure (XII) has been assigned on the basis of analogy.

When a mixture of the free base and the dione was refluxed in benzene solution with a little piperidine or trimethylamine, an oily neutral material was obtained, although in low yields, but no acidic product was formed under these conditions. When pyridine was added to the above mixture, the yield of the neutral condensation product improved remarkably (Howe *et al.*, *ibid.*, 1945, **67**, 381 ; Friedman and Robinson, *Chem. & Ind.*, 1951, 777 ; Newman, referred in the latter paper). Robinson and Newman used the above conditions to prepare the diketone (XIII) from 1-methyl-*cyclo*hexane-2 : 6-dione and diethylaminobutanone. The oily distillate from the condensation of the base (XV) with the dione was obtained in about 50-55% yield and consisted mostly of the triketo-ester (V). This distillate had a maxima at 250mμ in the ultraviolet (log ϵ 3.1) showing that only partial ring-closure had taken place in contrast to the case of diethylaminobutanone under identical conditions. This was, however, not very surprising considering the decreased acidity of hydrogen in $-CO-CH_2-$ compared to $CO-CH_3$. Ring-closure of the triketo compound to the bicyclic eneone (VI) could be effected by refluxing with aluminium *tert.*-butoxide in benzene solution (Wayne and Adkins, *J. Amer. Chem. Soc.*, 1940, **62**, 3401 ; Wendler, Slates and Tishler, *loc. cit.*) or by refluxing with piperidine acetate in benzene (Kuhn, *Ber.*, 1936, **69**, 98). Yields were roughly 25-30% in either case, although with the latter reagent a much cleaner product could be obtained. Wieland *et. al.* (*loc. cit.*) cyclised the same compound by refluxing with a mixture of triethylamine and benzoic acid in xylene solution, but did not report the yield. The bicyclic compound (VI) had the expected spectral properties and was further characterised by a 2 : 4-dinitrophenylhydrazone, m.p. 185-86°. Catalytic reduction of the double bond and hydrolysis of the resulting dihydro derivative (VII) afforded a gummy acid mixture from which two crystalline acids, m.p. 133-34° (VIIIa) and m. p. 121-24° (VIIIb) could be isolated (cf. Wieland *et al.*, *loc. cit.*).

For the elaboration of the third ring, we selected a method which was different from the Swiss procedure and had the advantage that the transformation could be

effected in only two steps and without isolation of the intermediates. The overall yield was also very good. The Swiss procedure required five to six steps for the same conversion. The diketo-acid, m.p. 133-34° (VIIIa) was refluxed with acetic anhydride and acetyl chloride to furnish the enol-lactone enol-acetate (XVII) which was obtained as an oil. This was next treated with the Grignard reagent from ethylmagnesium bromide, and the crude reaction product cyclised to the tricyclic diketone (IX) which could be directly obtained crystalline. After purification, this had m. p. 135-36° ($\lambda_{max}^{alcohol}$, 250 mμ ; log ε, 4.23; bands at 5.84μ, 6.0μ and 6.2μ in the infra-red). This method is analogous to the procedure of Fujimoto for the synthesis of progesterone labelled at C_4 position (*J. Amer. Chem. Soc.*, 1953, **75**, 3259). Reduction of the above diketone with sodium borohydride in alcohol yielded the corresponding diol which in the crude stage was oxidised with manganese dioxide in chloroform (Sondhiemer, Amendolla and Rosenkranz, *Exper.*, 1953, **9**, 62 ; *J. Amer. Chem. Soc.*, 1953, **75**, 5930) to the hydroxy-enеone (X), m.p. 132-33° ($\lambda_{max}^{alcohol}$, 250 mμ ; log ε, 4.13 ; bands at 2.8μ, 6.0μ and 6.2μ in the infra-red). The physical and spectral properties agree in all respects with the values reported by Wieland *et al.* (*loc. cit.*) for the diketone and the hydoxy-enеone prepared by them from the bicyclic acid, m.p. 133-34°. In view of the publications by the Swiss chemists our experiments with the isomeric acid, m.p. 123-24°, were not pursued.

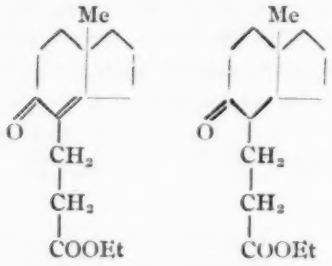
The configuration of the tricyclic diketone, m.p. 135-36° (IX) had been firmly established by the Swiss chemists (Wieland, Anner and Miescher, *Helv. Chim. Acta*, 1953, **36**, 646) which they later utilised for the total synthesis of D-homosteroids (Wieland, Uberwasser, Anner and Miescher, *ibid.*, 1953, **36**, 1231). The variants described by us in the present communication make available the above tricyclic compounds (IX and X), and hence, the D-homosteroids by one of the shortest routes so far described to synthesise steroids.

The condensation of the methoiodide of diethylaminobutanone with the sodio derivative of 1-methyl*cyclo*hexane-2 : 6-dione in presence of aluminium *tert.*-butoxide in methanol-benzene mixture afforded mostly neutral material from which the desired diketone (XIII) could be obtained by chromatography ; formation of acidic material was practically negligible, although the yield of the diketone was not very encouraging. The pyridine method has been described since no details have been published so far.

In the preparation of the Mannich base (XV : Chaudhuri and Mukharji, *loc. cit.*) further improvement in the yield has been effected by working up the mother-liquors left after removal of the crystalline base hydrochloride (XIV). We have used a revised nomenclature for this base (XV) in the present paper because the one used in our earlier publication is apt to be confusing.

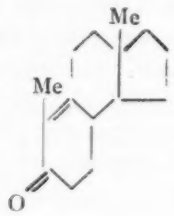
After our paper on the above Mannich base had been published, Nazarov and Zavyalov (*Chem. Abs.*, 1953, **47**, 5364) described that the product obtained by heating γ-acetobutyric acid with paraformaldehyde and dimethylamine hydrochloride, on esterification with methanolic hydrogen chloride, followed by basification with

potassium carbonate, yielded an unsaturated keto-ester, which on oxidation with nitric acid furnished succinic acid. On the basis of this they concluded that the reaction with paraformaldehyde had occurred at the methylene position, and they assigned structure (XVI) to their unsaturated ester. This is contrary to our observations, unless the change of the base hydrochloride, employed, in some peculiar way influences the reaction path, and this from all considerations appears very unlikely. We had no difficulty in obtaining the crystalline base hydrochloride (XIV) as well as the ethyl ester of the base (XV), which also analysed well. The structure of our product was very convincingly proved by conversion in to δ-ketoazelic acid. We are of the opinion that the oxidation with nitric acid, which the Russian chemists used, is somewhat too drastic and the possibility of further oxidation of glutaric acid to succinic acid under such conditions cannot be entirely ruled out.

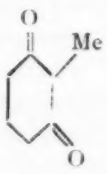


(I)

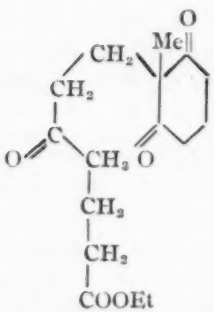
(II)



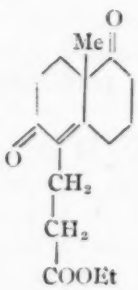
(III)



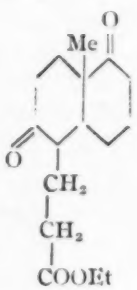
(IV)



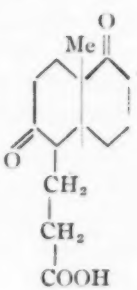
(V)



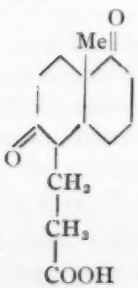
(VI)



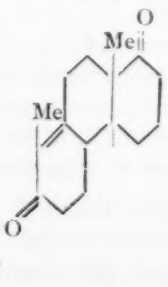
(VII)



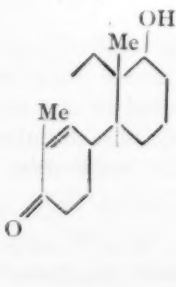
(VIII a)



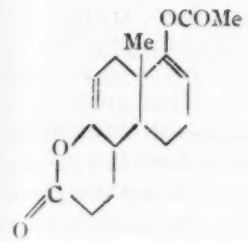
(VIII b)



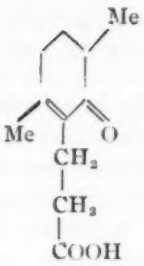
(IX)



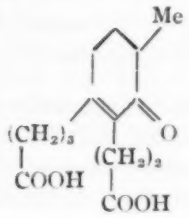
(X)



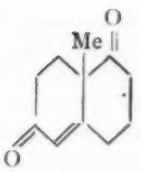
(XVII)



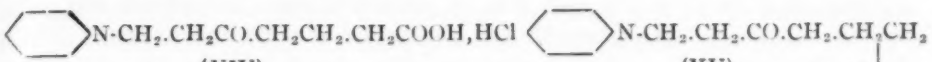
(XI)



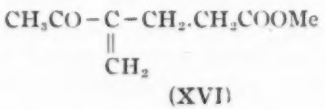
(XII)



(XIII)



(XIV) (XV)



(XVI)

EXPERIMENTAL

1-Methylcyclohexane-2:6-dione (IV) was best prepared by cyclisation of ethyl 4-ketohexane-1-carboxylate with alcohol-free sodium ethoxide in dry ether, initially at room temperature for about 3 hours, followed by reflux for another hour. An average yield was about 20 g. of dione from 34 g. of the keto-ester, m.p. 208-209°; lit. reports m.p. 210° (Blaise Maire, *loc. cit.*).

Ethyl 6-Piperidino-4-ketohexan-1-carboxylate (XV) was prepared as described in our previous communication (Chaudhuri and Mukharji, *loc. cit.*). A mixture of γ-acetobutyric acid (39 g.), piperidine hydrochloride (36.5 g.) and paraformaldehyde (9 g.) furnished on an average about 34-35 g. of the crystalline base hydrochloride, m.p. 158-59°, which was then converted into the above ethyl ester in the usual way.

However, considerable quantities of the base hydrochloride remained in alcohol-acetone solution which could not be recovered by direct crystallisation. The following procedure resulted in a fair recovery of the base as its ethyl ester. The alcohol-acetone solution obtained after removal of the crystalline base hydrochloride was completely evaporated to dryness under reduced pressure and the brown gummy residue esterified with 3% ethanolic hydrogen chloride. Excess of alcohol was then removed under reduced pressure. The residual viscous mass was dissolved in the minimum quantity of water and extracted three times with ether to remove the unchanged keto-acid. The aqueous solution was then carefully basified and the liberated Mannich base ethyl ester isolated by repeated ether extractions and purified by distillation. The structure of this product was also settled by conversion into δ-ketoazelic acid.

Condensation of Ethyl 6-Piperidino-4-ketohexan-1-carboxylate with 1-Methyl-cyclohexane-2:6-dione: Formation of 1-Methyl-1-(3'-keto 6-carbethoxy-hexyl)-cyclohexane-2:6-dione (V)

(*a*). To a solution of sodium methoxide in anhydrous methanol, obtained from metallic sodium (1.2 g.) and methyl alcohol (30 c.c.), the *cyclo*hexan-dione (6.3 g.) was added and left at room temperature to obtain a clear solution. It was then cooled in ice and a solution of the methoiodide of ethyl 6-piperidino-4-ketohexan-1-carboxylate, prepared from the base (15 g.), in absolute methyl alcohol was added. After allowing it to remain at this temperature for about 3 hours, it was left at room temperature overnight. Next day it was heated on a steam-bath for about an hour, then cooled and poured into ice containing some hydrochloric acid. The resulting solution was then saturated with ammonium chloride and extracted several times with ether. The ether extract was then washed with ice-cold 5% sodium bicarbonate solution until the aqueous extract was alkaline to litmus. The ether solution was washed with water, dried over anhydrous sodium sulphate and concentrated. The oil left on removal of the ether distilled at 170°-195°/1 mm. and a portion of this distillate solidified. This was identified as the unchanged dione, m.p. 208-209°. The remainder of the oil (about 1.0 g.) did not furnish any solid derivative and was not further investigated.

The bicarbonate extract was acidified with ice-cooling and the precipitated acid obtained as silky needles was collected by filtration and crystallised from hot water, m.p. 141-42°. This acid is soluble in hot water, but sparingly so in cold water. From potentiometric titration it was found to be dibasic. $\lambda_{max}^{alcohol}$, 250 mμ; log ϵ, 4.14. (Found: C, 62.5; H, 7.61. $C_{14}H_{20}O_5$ requires C, 62.68; H, 7.46 per cent).

(*b*). A mixture of 1-methyl*cyclo*hexan-2:6-dione (12.6 g.), ethyl 6-piperidino-4-ketohexan-1-carboxylate (30 g.), dry pyridine (10 c.c.) and benzene (100 c.c.) was heated under reflux for five hours. The reaction mixture was then cooled and acidified with ice and HCl. The unchanged dione separating was removed by filtration. The benzene layer was then separated and the aqueous layer once extracted with ether and the extract combined with the first benzene extract. The combined solution was then washed with cold 5% sodium bicarbonate solution, cold dilute HCl solution and finally with water. The solvent was then removed under reduced pressure and the residual oil distilled. After a small forerun of the low boiling material, the oily product distilling over at 185°-190°/1 mm. was collected, yield 12 g. (53% based on reacted dione). This distillate had $\lambda_{max}^{alcohol}$, 250 mμ (log ϵ, 3.1) showing that partial ring-closure had taken place during condensation. Attempts to purify the adduct by redistillation almost in every case produced some *cyclo*hexan-dione, possibly by reversal of the Michael at elevated temperature. The adduct, however, very readily furnished a trisemicarbazone which after crystallisation from a large volume of alcohol had m.p. 203°-209°, depending on the rate of heating. (Found: C, 48.58; H, 7.2; N, 27.36. $C_{19}H_{33}O_5N_9$ requires C, 48.82; H, 7.07; N, 26.98 per cent). The bicarbonate extract on acidification yielded the dibasic acid, m.p. 141-42° in about 5% yield.

9-*Methyl*-4-(*β-carbethoxyethyl*)-Δ^4-*octalin*-3 : 8-*dione* (VI).—(*a*). The above triketo-ester (7.4 g.) and aluminium *tert.*-butoxide (8 g.) in dry benzene were refluxed for 40 hours under nitrogen. The reaction mixture was then cooled, decomposed with ice and HCl and the organic layer separated. The aqueous layer was extracted once more with ether and the ether extract combined with the first benzene extract. The combined extract was washed with water and carefully decanted off from the tarry matter that had separated; after washing with dilute sodium bicarbonate solution and with water, this was dried and concentrated under reduced pressure. The residual viscous oil distilled at 170°-180°/1 mm. which on redistillation boiled at 172-75°/1 mm., yield 1.8 g. $\lambda_{max}^{alcohol}$, 250 mμ; log ε, 4.15. (Found: C, 68.52; H, 8.3. $C_{16}H_{22}O_4$ requires C, 69.06; H, 7.91 per cent). This enedione furnished a *bis*-2 : 4-dinitrophenylhydrazone which after three crystallisations from ethyl acetate had m.p. 185-86°. (Found: C, 52.41; H, 4.85; N, 17.45. $C_{28}H_{30}O_{10}N_8$ requires C, 52.66; H, 4.7; N, 17.53 per cent).

(*b*). The triketo-ester (7.4 g.) was heated with a mixture of piperidine (2.1 g.) and glacial acetic acid (3 c.c.) in benzene (40 c.c.) in a flask fitted with a Dean-Stark water separator. After reflux for 40 hours under nitrogen, the reaction product was worked up as described above. The distillate (2 g.), b.p. 172°-176°/1 mm. had identical ultraviolet absorption spectra as above and also furnished the same 2 : 4-dinitrophenylhydrazone.

9-*Methyl*-1 : 6-*diketodecalin*-5-*β-propionic Acid* (VIIIa & VIIIb).—The unsaturated compound (VI, 10 g.), obtained above, in ethanol (15 c.c.) was reduced at room temperature with hydrogen in presence of 10% Pd—C (0.5 g.). In about 10 hours the theoretical amount of hydrogen was absorbed. The catalyst was filtered off, the solvent removed and the dihydro derivative (VII) purified by distillation, b.p. 170-72°/1 mm., yield 9 g. This distillate did not show any absorption around 250 mμ in the ultraviolet.

This reduced product (8 g.) in methanol (35 c.c.) was treated with 5% NaOH solution (30 c.c.), left at room temperature for about 90 minutes and then it was heated for a short period at 80°, treated with a few drops of HCl (dil.) and concentrated under reduced pressure. The residue was acidified with cooling and the organic matter taken up in chloroform. The gummy acid left on removal of the chloroform was dissolved in dry ether and on allowing it to stand for some time a portion of the gum crystallised. These were filtered off, washed with cold dry ether and had m.p. 129-32°. After two crystallisations from ether this had m.p. 134-35°, yield 3.4 g. (Found: C, 66.21; H, 7.75. $C_{14}H_{20}O_4$ requires C, 66.67; H, 7.91 per cent). From the mother-liquors it was somewhat difficult to obtain a pure specimen of the other isomer directly, although a few crystals could be obtained. The gum therefore was re-esterified, sublimed and hydrolysed as described above. The resulting gummy acid was dissolved in a mixture of acetone and ether and cooled when some crystals appeared. After a second crystallisation from acetone-ether mixture it had m.p. 123-24°, yield 1.5 g.

1 : 7-*Diketo*-8 : 11-*dimethyl*-$\Delta^{8:14}$-*dodecahydrophenanthrene* (IX).—The acid of m.p. 134-35° (2.5 g.), acetic anhydride (12 c.c.) and acetyl chloride (12 c.c.) were refluxed under nitrogen for about 50 hours. The low boiling materials were then carefully removed under diminished pressure and the residue sublimed when a viscous oil came over at 180°-185°/1 mm., yield 1.8 g. This oily enol-lactone enol-acetate (XVII) did not solidify on standing or on trituration with solvents.

The above enol-lactone enol-acetate (1.7 g.) in dry ether (80 c.c.) was cooled in ice-salt mixture and ethylmagnesium bromide, prepared from magnesium (0.2 g.) and ethyl bromide (0.6 g.) in ether (25 c.c.), was added with stirring. A curdy white precipitate was obtained. At the end of the addition, the mixture was slowly allowed to attain room temperature and left as such overnight. It was then decomposed with a cold solution of ammonium chloride and the organic layer separated ; the aqueous layer was extracted three times with ether and combined with the first ether extract and then concentrated. The residue left after removal of the ether was treated with glacial acetic acid (32 c.c.) and HCl (conc., 3 c.c.) and left in an atmosphere of nitrogen at room temperature for 48 hours. It was then all but completely evaporated to dryness under reduced pressure, diluted with water and extracted with ether. The ether extract was then washed with cold dilute NaOH solution, water and dried over anhydrous sodium sulphate. On allowing the ether to evaporate slowly, crystals were deposited which were collected by filtration. This crude diketone had m.p. 128-31° and was slightly coloured. A benzene solution of the compound was passed through a small amount of alumina and the crystals from this were recrystallised from dry ether, m.p. 135-36°, yield 0.6 g. $\lambda_{max}^{alcohol}$, 250 mμ ; log ε, 4.23 ; bands at 5.84μ, 6.0μ and 6.2μ in the infra-red. (Found : C, 77.82 ; H, 9.12. $C_{16}H_{22}O_2$ requires C, 78.05 ; H, 8.94 per cent).

1-*Hydroxy*-7-*keto*-8 : 11-*dimethyl*-$\Delta^{8:14}$-*dodecahydrophenanthrene* (X).—The above diketone (300 mg.) in alcohol (2-3 c.c.) was added to a solution of sodium borohydride (500 mg.) in 70% ethyl alcohol (10 c.c.) with ice-cooling and then allowed to attain room temperature and left as such overnight. Next morning the solution was evaporated to dryness, diluted with water and extracted several times with chloroform. The residue from chloroform was an amorphous mass which did not show any absorption around 250 mμ in the ultraviolet. Bands around 5.84μ and 6.0μ in the infra-red were also absent. This amorphous material in chloroform (7-10 c.c.) was stirred overnight with manganese dioxide (200 mg.) at room temperature. The oxide was then filtered off, washed with several portions of hot chloroform and the total chloroform extracts were combined and concentrated. The gummy residue was dissolved in dry benzene and passed through a short column of alumina and concentrated. The resulting crystalline product was crystallised from benzene-petrol ether mixture, m.p. 132-33° ; $\lambda_{max}^{alcohol}$, 250 mμ ; log ε, 4.1 ; bands at 2.8μ, 6.0μ and 6.2μ in the infra-red. (Found : C, 77.13 ; H, 9.72. $C_{16}H_{24}O_2$ requires C, 77.42 ; H, 9.68 per cent).

Condensation of 1-*Methylcyclohexane*-2 : 6-*dione with Diethylaminobutanone*

(*a*). The dione (6.3 g.) was added to a solution of sodium (1.2 g.) in methanol (30 c.c.) and left for some time. It was then cooled in ice and a methanolic solution

of the methoiodide of diethylaminobutanone, prepared from the base (10 g.), was slowly added. The mixture was left overnight and then refluxed for 1 hour, cooled and worked up in the usual way and separated into neutral and acidic fractions. The neutral fraction distilled over a range of 120°-135°/1 mm. and the yield was about 2.0 g. No solid derivatives could be prepared from this fraction. (Found: C, 65.69; H, 8.38 per cent).

The acidic portion, which was obtained initially as an oil, solidified on distillation, yield 4.0 g., m.p. 46-47°; $\lambda_{max}^{alcohol}$, 243 mμ; log ε, 4.1. (Found: C, 67.12 H, 8.32. $C_{11}H_{16}O_3$ requires C, 67.35; H, 8.16 per cent.). The *semicarbazone* after crystallisation from dilute alcohol had m.p. 201-203°. (Found: N, 16.84. $C_{12}H_{19}O_3N_3$ requires N, 16.6 per cent). The corresponding ethyl ester afforded a red 2:4-dinitrophenylhydrazone, m.p. 101-102°. (Found: N, 14.02. $C_{19}H_{24}O_6N_4$ requires N, 13.86 per cent).

(*b*). This procedure was exactly as the one above excepting that before the addition of the methoiodide, a solution of aluminium *tert.*-butoxide (10 g.) in dry benzene was added. The reaction mixture was worked up the usual way and separated into acidic and neutral fractions. The neutral portion (about 7 g.) was separated into two fractions by distillation: (*i*) b.p. 115°-120°/1 mm., a mobile liquid, 3 g., (*ii*) b.p. 128°-132°/1 mm., a somewhat viscous liquid, 3 g. The second fraction was chromatographed over alumina and eluted with a mixture of benzene and ether. The crystalline material thus obtained was recrystallised from ether-petrol ether mixture, m.p. 48-49°; $\lambda_{max}^{alcohol}$, 244 mμ; log ε, 4.08. (Found: C, 73.85; H, 8.1. $C_{11}H_{14}O_2$ requires C, 74.16; H, 7.86 per cent). Yield of the crystalline product was about 2 g. The *bis*-semicarbazone was crystallised from alcohol and then had m.p. 244-45°. (Found: N, 29.08. $C_{13}H_{20}O_2N_6$ requires N, 28.77 per cent).

The first fraction of the distillate did not solidify and also did not afford any crystalline derivative.

(*c*). A mixture of the dione (6.3 g.) diethylaminobutanone (7.5 g.), dry pyridine (5 c.c.) and benzene (50 c.c.) was refluxed for about 6 hours in a flask fitted with a Dean-Stark water separator. The mixture was then cooled and poured into a mixture of ice and HCl. It was then filtered from a precipitate (about 1.3 g.) which was the unchanged dione. The aqueous solution was removed and extracted with ether and this extract was then mixed with the original benzene solution. The combined extract was then washed with cold 5% sodium bicarbonate solution, then with water and finally concentrated under reduced pressure. The residue left after removal of the solvent distilled at 128°-130°/1 mm. and the distillate solidified on scratching. It was recrystallised from ether-petrol ether mixture, m.p. 48-49°, yield 3.5 g. The *bis*-semicarbazone had m.p. 244-45° and identical with the sample obtained above.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA
AND
DEPARTMENT OF CHEMISTRY,
KARNATAK COLLEGE,
DHARWAR.

Received April 30, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

ION EXCHANGE BEHAVIOUR OF RESORCINOL-FORMALDEHYDE RESIN

By S. L. Gupta

The exchange capacity of the acid-catalysed and thoroughly cured (10 hrs. at 100°-110°) resorcinol-formaldehyde resin was determined both by analytical and potentiometric titration methods for finer fractions, the fineness extending up to colloidal range. The results of a number of determinations for different particle sizes of the resin suspensions show a limiting value close to 1220 m.e. per 100 g. of the resin, representing the theoretical value on the assumption that the exchange spots (two -OH groups in this case) are hydrated. The limiting value was found to be the same irrespective of the valency of the cations adsorbed. Also, it was possible to identify the two -OH groups by a small but definite inflexion at the middle of such titration curves.

The exchange isotherms show definite inflexions in the curves obtained, indicating that the ions are held with different intensities of adsorption on the resin surface corresponding to the two -OH groups in the resorcinol unit and also indicate that the bivalent cations are more firmly held on to the resin surface than the monovalent cations.

According to the structure of the phenol-formaldehyde resins postulated by Houwink ("Physik. Eigenschaften und Teinbace von Natur und Kunsthazen", p. 119, 1934) and accepted by later investigators, the functional groups are supposed to remain intact after polymerisation. It is therefore possible to bring these groups into reaction with added reagents. Depending upon the nature of the reacting groups, the method of investigation may be modified in order to characterise the group or groups. Thus, for instance, the acid form of the phenol-formaldehyde resin can be potentiometrically titrated and from the inflexions, the nature of the hydrogen ions associated with the resin may be roughly estimated. It is further assumed that the functional groups are spatially unhindered and are accessible from all sides. To render this and to make the assumption safer, the resins may be taken in the colloidal form.

The present investigation is concerned with the study of the exchange behaviour including potentiometric curves of resorcinol-formaldehyde resin which is supposed to have two functional groups.

Experimental

The resin was prepared according to the method of Adams and Holmes (*J. Soc. Chem. Ind.*, 1935, **54**, 1T). The loose, soft aggregates of the washed and cured (at 100°-110° for 10 hrs.) resin were broken by light grinding. The colloidal fractions of the resin were isolated by allowing aqueous suspensions of the −200 mesh resin to settle for 20 hours and 8 hours respectively and syphoning the materials remaining above a height of 7 cm. In order to ensure complete removal of bases, these were first collected in $N/20$-HCl medium. The suspension was afterwards filtered through sintered glass, washed free of HCl and resuspended in conductivity water.

Procedure.—The interaction between the acid resin and alkali was followed potentiometrically as well as by direct chemical determination. From a knowledge of the

exchange capacity, thus obtained, it was possible to saturate fine suspensions, *i.e.* to form 'Resinates', with different cations by adding equivalent amounts of the bases to the resin systems and allowing them to attain equilibrium. The saturating cations were then exchanged with several other different cations.

Sodium was estimated either gravimetrically (Barber and Kolthoff, *J. Amer. Chem. Soc.*, 1928, **50**, 1625) as triple acetate, $NaZn(UO_2)_3.(C_2H_3O_2)_9$, or volumetrically (Dobbing and Byrd, *ibid.*, 1931, **53**, 3288) by titrating the solution of the triple acetate with standard alkali using phenolphthalein as an indicator. Barium was determined as $BaSO_4$. Calcium was precipitated as calcium oxalate and titrated in presence of H_2SO_4 with a standard $KMnO_4$ solution. Ammonium ion was estimated after nesslerisation by comparing the colour developed with a standard ammonium chloride solution. A Leeds and Northrup type K potentiometer was used for E.M.F. measurements.

Exchange of Cations adsorbed from Bases.—The alkali adsorption was studied by adding an excess of standard alkali in weighed amounts of the resin kept in well-stoppered Jena bottles. The mixtures were shaken for definite periods in an end-to-end shaker. After allowing the solid matters to settle, an aliquot portion of the supernatant alkali was titrated with acid using a suitable indicator. The amount of alkali taken up by the resin was expressed in milliequivalents (m.e.) per 100 g. of it. All precautions were taken to prevent entry of CO_2. The supernatant liquids were generally coloured (Gupta, Bose and Mukherjee, *J. Phys. & Coll. Chem.*, 1950, **54**, 1098) owing perhaps to the solubilisation of a portion of the resin in presence of alkali. On account of the colour of the solution Wesselow's mixed indicator (p_H 5.0-6.5) and bromothymol blue (p_H 6.0-7.6) were used for titration. The results are shown in Table I.

TABLE I

Wt. of 100 mesh resin.	0.0925 *N* NaOH.	Exchange capacity with Wesselow's indicator.	(B.T.B.) indicator.
0.0322 g.	50 c.c.	924 m.e.	1215 m.e.
0.0329	100	905	...
0.0589	50	942	1330
0.0586	100	877	1294
0.0944	50	917	...

Phenolphthalein was, however, a suitable indicator if barium and calcium hydroxides were used for adsorption and subsequent titrations. This is due to the fact that the bivalent ions keep the highly dispersed but slightly solubilised resin in a coagulated state. The results obtained with a 200 mesh sample are shown in Table II.

TABLE II

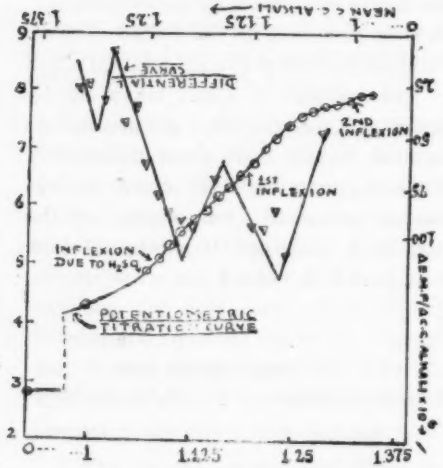
Expt. No.	Wt. of resin.	Exchange capacity (m.e.)
1	0.2232 g.	1160 $[Ba(OH)_2]$
2	0.9460	1360 $[Ca(OH)_2]$

In this connection, experiments of Akeroyd and Broughton (*J. Phys. Chem.*, 1938, **42**, 343) may be mentioned in which they observed as high as 3600 m.e. exchange capa-

city of the bifunctional resin using $Ca(OH)_2$. They suggested that lime was probably taken up as -CaOH. While this possibility is not ignored, it is not borne out by the present work. It must be mentioned that a small error was introduced in the above experiments in not taking sufficient precautions against carbon dioxide of the air.

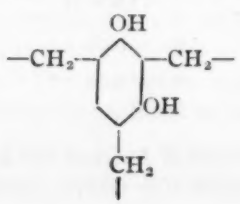
Potentiometric Titration of the Supernatant Solution of the Alkali-treated Resin.— Partly because the supernatant liquid containing the dispersed portion of the resin was too much coloured to enable accurate indicator method of colorimetric titration and partly because it was difficult to select a suitable indicator, the excess of alkali was potentiometrically titrated. For this purpose, a sample of resin, cured for 10 hours, was taken in a 250 c.c. Jena bottle and after addition of 75 c.c. of an approximately N/10-NaOH solution and shaken in an end-to-end shaker for 12 hours. The mixture was then allowed to settle for a day and 10 c.c. of the supernatant liquid was withdrawn into the titration vessel containing an excess of H_2SO_4 of known strength (approx. 0.1 *N*). The excess of the acid was then potentiometrically titrated with NaOH using quinhydrone electrode. Therefore we are dealing here with a mixture of H_2SO_4 and a much weaker acid, *i.e.* hydrogen resin, for titration. The neutralisation points are better shown up by the buffer capacity curve (Fig. 1); the two peaks in this curve besides that of H_2SO_4 correspond to the neutralisation of the resin. This, as will be shown later, is an important characteristic of this resin. In the experiment 0.0834 g. of the resin was treated with 75 c. c. of 0.1069 *N*-NaOH, 10 c.c. of the supernatant solution was added to 10 c.c. of 0.1082*N*-H_2SO_4 and the mixture required 1.32 c.c. of 0.1069*N*-NaOH for neutralisation, corresponding to the second peak. On evaluation exchange capacity comes out to be equal to 1153 m.e. per 100 g. of the resin.

FIG. 1



DISCUSSION

The Significance of the Exchange Capacity.— According to Houwink's picture the structural unit of the resorcinol-formaldehyde resin may be represented as



The two (-OH) groups represent those belonging to the resorcinol unit which, since they do not take part in the condensation, remain intact. They are considered as the exchange spots on the resin. The linkages to other units of the structure take place through the methylene groups which are shared by two such adjacent units. Assuming that all the -OH groups are available for exchange, each unit having a weight of 128 g. ($C_6H_3O_2 + \frac{3}{2}CH_2$, only half of each $-CH_2-$ group being considered as part of each unit) will contain therefore 2 equivalents. Calculating on the basis of 100 g. of the resin, the exchange capacity becomes equal to 1560 m.e.

In none of the experiments including those to be presented later on, a value as high as 1560 m.e. could be attained. If, however, we assume that the H^+ ions on the exchange spots of the oven-dried resin (105°) exist not as H^+ but as H_3O^+ ion, the calculated exchange capacity becomes equal to 1220 m.e., a value close to the observed highest values. The existence of H_3O^+ ions in aqueous solutions of acids is now well established. It has been shown that in the case of colloidal clay acids the hydrogen ions are possibly present as H_3O^+ ions (Ganguli and Gupta, *Science & Culture*, 1948, **14**, 81). Existence of H_3O^+ ions in exchange resins has also been suggested by Boyd *et al.* (*J. Amer. Chem. Soc.*, 1947, **69**, 2818) in order to explain the easy exchange of hydrogen ions from the Amberlite IR-1, studied by them.

Exchange Capacity from the Direct Estimation of the Adsorbed Cation.—Instead of determining the amount of caustic soda consumed by the resin, the amount of sodium adsorbed by the resin may be directly estimated. For this purpose approximately 1 g. of the 10 hour-cured, 200 mesh sample of the resin was thoroughly shaken with an excess of 0.1*N*-NaOH for 12 hours, the total contact being 48 hours. This was then filtered through a Gooch crucible and leached with a further quantity of 0.1*N*-NaOH solution in order to completely replace the H^+ ions with Na^+. The Na resin, thus formed, was washed several times with alcohol which had been neutralised with NaOH. The Gooch with its contents was dried at 105° and the dry Na-resin lightly powdered. Portions of this Na-resin were then treated with 0.5*N*-HCl and shaken for 12 hours. The resin after filtration through a Gooch was further leached with 0.5*N*-HCl to completely replace the adsorbed Na^+. The Na^+ in the hydrochloric acid leachate was then estimated by titrating the sodium zinc uranyl acetate with NaOH. From the amount of sodium the exchange capacity per 100 g. of the resin was calculated (last column of Table III).

TABLE III

Na-resin.	H-resin left.	Exchange capacity.
0.0366 g.	0.0282 g.	1229 m.e.
0.0566	0.0423	1209

Table III shows the amount of Na-resin taken for the estimatian of adsorbed Na^+ and also the corresponding amount of H-resin left behind. All the samples were dried at 105°. Assuming some arbitrary degree of hydration of the Na^+ and H^+ ions, the following ratios between the weights of Na-resin and H-resin have been calculated. The results together with the experimental values are shown in Table IV.

TABLE IV

$\frac{Na_2R}{(H_2O)_2R}$	$\frac{Na_2(H_2O)_2R}{(H_2O)_2R}$	$\frac{Na_2(H_2O)_4R}{(H_2O)_2R}$	Experimental values.
1.05	1.27	1.49	(a) 1.30
			(b) 1.34

The experimental values are closer to the case in which both the H^+ and the Na^+ ions are each hydrated with one molecule of water (column 2). It is possible that Na^+ ions, which are usually hydrated with a larger number of water molecules, have lost most of them at the temperature of the measurement, viz. 105°. The hydration of the three dimensional resins, in which the linkage is through carbon atoms, is likely to be less favourable than the layer lattice siliceous clays. Perhaps for this reason the hydration of the exchangeable cations associated with the resins is also affected, and hence, the lower hydration of Na^+, as is shown by the above data.

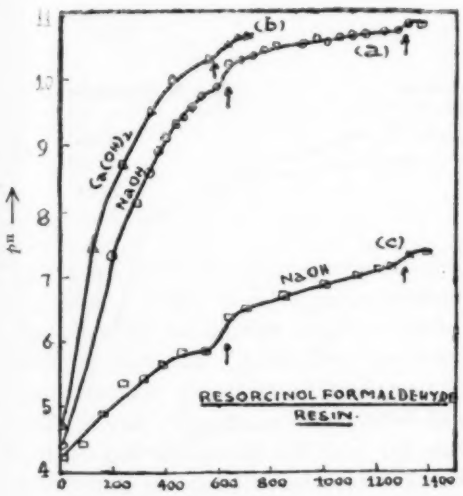
Potentiometric Titration of the Acid-resin with Alkali.—The interaction of the coarse-grained resin with alkali is a slow process, but preliminary experiments have shown that the colloidally dispersed resin acid can be successfully titrated with alkali and the neutralisation reaction is rapid enough for potentiometric measurements. For these experiments two suspensions of the finely dispersed material were prepared from portions not settling in 20 hours and 8 hours respectively.

The curve shown in Fig. 2 (curve a) was obtained by titrating a 20 hour-suspension of the acid resin (0.58 g./litre) with 0.1069*N*-NaOH using the hydrogen electrode. The resin after each addition of alkali was vigorously stirred and the E.M.F. remaining constant for 10 to 15 minutes was read as the equilibrium value. It will be seen from the neutralisation curve that it is characterised by two inflexion points. The inflexions are small but fairly marked. Mention has been made earlier that these two inflexions correspond to the neutralisation of the two exchangeable H^+ ions at the two -OH spots of the resorcinol-formaldehyde resin. The acidity corresponding to the first inflexion point is almost exactly half of that corresponding to the second. The resin suspension simulates a dibasic acid character. Corresponding to the second inflexion point, the exchange capacity is equal to 1237 m.e. The apparent pK values of the acid resin are 8.65 and 10.5 respectively. It may be of interest to know how resorcinol itself would behave under similar circumstances. Fig. 3 shows the titration curve of the pure resorcinol, obtained with the help of a Beckmann p_H meter fitted with glass electrode. The close similarity between the two curves is striking, but from the pK values calculated from the half neutralisation points (9.1 and 10.7) it appears that the resin acid is perhaps slightly stronger than pure resorcinol. Also, the acidity of the resorcinol calculated from the second inflexion point corresponds to the formula $C_6H_4(OH)_2$, where the H^+ ions in the phenolic -OH groups are unhydrated unlike that in the resin made from it.

The neutralisation curve, shown in Fig. 2 (curve c), refers to the resin material obtained by dialysis of the coloured extract of the alkali-treated, 10 hour-cured, coarse

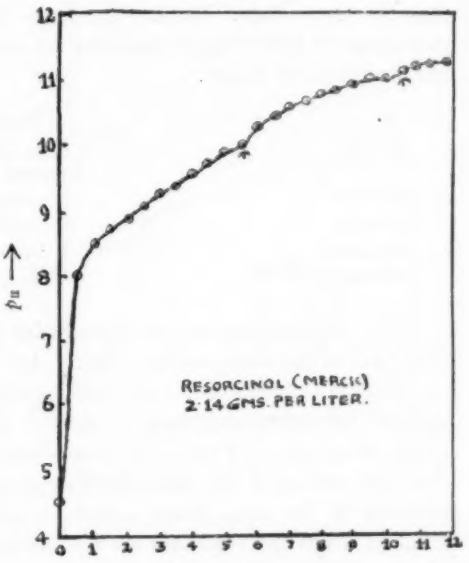
resin. The resulting acid sol (0.36 g./litre) was a reddish brown, stable, colloidal solution. The potentiometric titration was carried out with the help of hydrogen electrode. The titration curve shows two inflexions but at lower p_H's, as compared with the 20 hours' suspension. The exchange capacity corresponding to the second inflexion point is equal to 1250 m.e./

FIG. 2



Conc. of added alkali (m e./100 g.).

FIG. 3



c.c. of added alkali (0.0 945*N*) to 25 *c.c.*

Exchange Capacity from Interaction with Alkaline Earth Hydroxides.—Baryta and calcium hydroxide afforded higher exchange capacities than sodium hydroxide with coarse resin. The value was close to the theoretical in the case of the baryta and slightly higher in the case of calcium hydroxide. The possibility of the latter being adsorbed as -CaOH was mentioned by Akeroyd and Broughton (*loc. cit.*). In order to eliminate the effect of carbon dioxide, if any, a titration with calcium hydroxide using the 8 hours' suspension of the acid resin (0.61 g./litre) was carried out potentiometrically by means of hydrogen electrode. The titration (Fig. 2, curve b) was carried out up to the first equivalence point. Thus, there was only one inflexion and the exchange capacity, calculated from double the amount required to reach the first inflexion, is equal to 1210 m.e./100 g. Due to elimination of the effect of carbon dioxide, since under the condition of the experiment carried out in an atmosphere of hydrogen gas, the calculated exchange capacity is slightly lower and is very close to the theoretical exchange capacity. It further shows that calcium hydroxide does not react with the resin acids as -CaOH to any extent.

A comparison of the three curves (Fig. 2) reveals that both the half neutralisation p_H or the pK values and the p_H at which complete neutralisation occurs are lower, the

smaller the size of the particles in the suspension, or, in other words, for the same quantity of the resin the finer fraction exhibits stronger acid function.

Hydrolysis of the Resinates.—The resinates are hydrolysed in aqueous solution to different extents depending on the nature of the cation and, as such, resemble the salts of weak acids. It was observed that the hydrolysis was considerably suppressed in presence of a high cationic concentration. The results recorded in Table V show that the dilute suspensions (0.9293g./litre) of Na- and NH_4- resinates are more hydrolysable than the Ca-resinate. Unlike the latter the Ba-resinate hydrolyses appreciably. The percentage of hydrolysis of the different resinates at the low concentration of 11.3 m.e. per litre is shown below.

TABLE V

System.	Conc. of cation in supernat soln. in 60 c.c.	% Dissociation.
Na-Resin	0.3147 m.e.	46.28
Ca-Resin	0.1879	27.63
NH_4-Resin	0.3484	51.24
Ba-Resin	0.3702	54.44

The experiments were performed with 60 c.c. of the suspension containing 0.05576 g. of H-form of the resin (0.9293 g./litre), *i.e.* containing $0.05576 \times 12.2 = 0.68$ m.e. in 60 c.c.

Exchange Isotherms.—To equal volumes of the resinates having the same colloid content increasing quantities of neutral electrolytes were added. The concentration of the latter generally varied from one-fourth to four times the symmetry concentration. The final volume of the supernatant solution with colloid was in all cases 60 c.c. The analyses of the supernatant liquids were made for both the interacting cations after allowing about two weeks for the equilibriation. The experimental data are graphically illustrated in Figs. 4 to 7.

FIG. 4

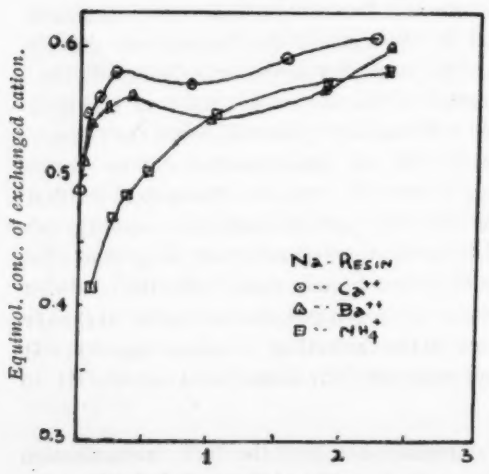
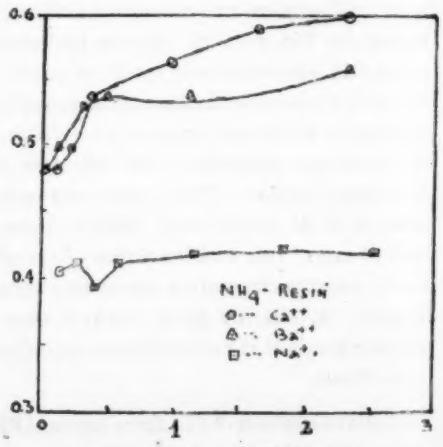


FIG. 5



The curves apparently do not look like the usual exchange adsorption isotherms. On the other hand, they show marked bends or inflexion points. These inflexions are more marked in those cases where the exchange is of a bivalent cation in the resinate for a monovalent one of the added electrolyte.

FIG. 6

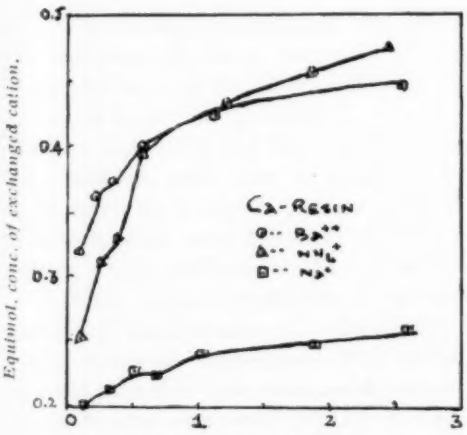
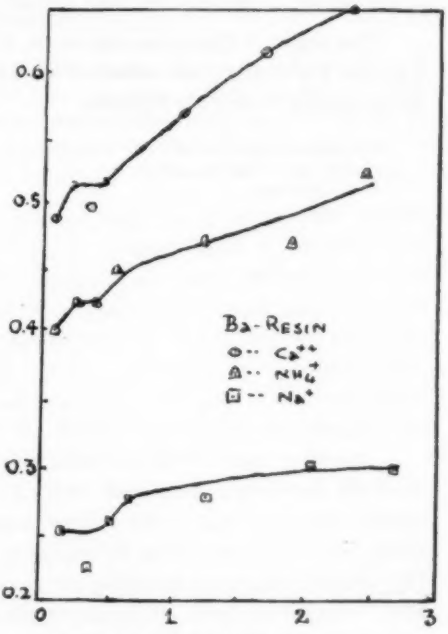


FIG. 7



A proper evaluation of the isotherms can be made in the light of the titration curves reported earlier. The latter have definitely demonstrated the existence of two types of exchange spots varying in their energy of adsorption. It is clear that the cations saturating the resin must have different degrees of exchangeability as a result of the different intensities of bonding of cations on the resin surface. The inflexion points in the isotherms indicate to a greater or less extent this property of the cations. It is to be expected that the differernce in the exchangeability will be more easy to follow in cases where the exchangeable cations are comparatively difficult to replace. That this is so is shown by the sharper inflexion points in the curves obtained from the calcium and the barium resins. It is, however, to be noted that in order to establish these inflexions, it is expedient to study the isotherm at an extremely low concentration and follow it up to a relatively high concentration of the added electrolytes. For this reason the electrolytes in these experiments were added at one-fourth of the symmetry concentration, increasing gradually to four times the symmetry concentration.

It will be noticed from these curves that the inflexions occur at the low concentration region and almost at the same equilibrium concentration of the added electro-

lytes for each of the systems. For the systems saturated with the divalent cations this equilibrium concentration is almost the same, but higher than that for the monovalent cation-saturated systems. This follows from the fact that the divalent cations, corresponding to the same region of the exchange spots, are probably more firmly held by such forces as determine their adsorbability and therefore require a larger concentration of the added electrolytes for their replacement.

The author's thanks are due to Dr. S. K. Mukherjee, D.Sc., Lecturer in Chemistry, Calcutta University, for constant encouragement during the progress of the work and for providing laboratory facilities.

University College of
Science and Technology,
Calcutta.

Received April 1, 1955.

[Jour Indian Chem. Soc., Vol. 33, No. 2, 1956]

STEROID COMPOUNDS. PART VI. SOME EXPERIMENTS TOWARDS THE SYNTHESIS OF 11-KETO STEROIDS

By P. C Mukharji

The base-catalysed condensation of ethyl 4-keto-2 :3-dimethyl*cyclo*hexene-1-carboxylate with alkyl halide and vinylmethyl ketone has been studied. An extension of this reaction to ethyl 4-keto-3-methyl-2-furyl*cyclo*hexene 1-carboxylate to obtain intermediates that could be useful for synthesis of 11-keto steroids broke down because the reaction with vinylmethyl ketone did not yield the desired compound (XVIII).

The present investigation was started in 1951 to find out a convenient method of obtaining the furan derivative (XVIII). This compound being a derivative of furacrylic acid, on the Marckwald cleavage (Marckwald, *Ber.*, 1887, **20**, 2813) could be expected to produce the diketo-dicarboxylic ester (I). The tricyclic compound (II) or its various derivatives like (III) could be easily obtained from the above ester (I) and these intermediates could then be profitably utilised for the synthesis of 11-keto steroids. The synthetic approach appeared to be of great promise, provided that a convenient synthesis of the furan derivative (XVIII) could be found. Although our attempts to obtain it were unsuccessful, the results have been of some interest in other respects.

Of the several possibilities to synthesise (XVIII) that were considered, the base-catalysed condensation of vinylmethyl ketone with ethyl 4-keto-3-methyl-2-furyl-Δ^2-*cyclo*hexene-1-carboxylate (VII) appeared to be one of most promise. The anion derived from this compound could react at either of the positions 1 or 3, to furnish (IX) or the bicyclic compound (XVIII : R′=Et) *via* the intermediate diketone (XIII). The compound (VII) is a vinylogous β-keto-ester and closely related to Hagemann's ester (IV). It has been well established that alkylation of Hagemann's ester takes place at the position 3, next to the keto group (Smith and Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 631; Horning *et al.*, *ibid.*, 1949, **71**, 1771). This is what one would expect in a compound of this structure ; for in the mesomeric anion derived from it, reaction is most likely to take place at position-3 which is not substituted compared to position-1, carrying a substituent. The same situation, however, does not obtain in the compounds (V) and (VII) where both the positions 1 and 3 carry substituents. A mixture of products derived from condensation at both the positions could be expected in any base-catalysed reaction. However, the keto group being somewhat more electron-withdrawing, compared to the ester group, it was thought that in the mesomeric anion, derived from such a system, the electron density would be higher in the vicinity of the keto group (Birch, *J. Chem. Soc.*, 1950, 1551, 2325) and the product derived from reaction at position-3 would very likely predominate in the mixture. As far as could be found in literature, there are no reports on reactions of compounds of this type (V and VII).

A preliminary study with the readily available derivative, ethyl 4-keto-2 : 3-dimethyl-Δ^2-*cyclo*hexene-1-carboxylate (V), was therefore undertaken. An examination of the structure of the two possible compounds that could arise from it reveals that

the compound derived from reaction at position-3 will no longer be a vinylogous β-keto-ester in contrast to the other isomer derived from reaction at position-1, where the vinylogous β-keto-ester system will prevail. By suitable treatments, *i.e.* hydrolysis followed by decarboxylation, such mixtures can be easily separated into acidic and neutral components. Reaction of the above ester (V) with methyl iodide in presence of potassium *tert.*-butoxide in *tert.*-butyl alcohol was very rapid and practically over at room temperature. The crude reaction product was hydrolysed with dilute KOH solution and the total acidic material decarboxylated by heating with dilute HCl. The resulting mixture could be separated into two portions, one acidic and the other neutral, in almost equal amounts. The neutral fraction was a colorless mobile liquid with a very strong ketonic smell, which readily furnished a semicarbazone, m. p. 210° and a red 2 : 4-dinitrophenylhydrazone, m.p. 165°. It can be best represented as 2 . 3 : 4-trimethyl Δ^2-*cyclo*hexenone (XIV). The acidic portion was initially obtained as a gum which soon solidified, and after purification had m. p. 120°. The corresponding methyl ester (XIa) was characterised by a semicarbazone, m. p. 143.5°. The acid can be best represented as 4-keto-2 : 3 : 3-trimethyl*cyclo*hexene-1-carboxylic acid (XI).

The next reaction studied was the condensation of the potassium enolate of (V) with vinylmethyl ketone. The crude reaction product was treated as described in the previous case and separated into acidic and neutral components in almost equal amounts. The acid (m. p. 162° ; $\lambda_{max}^{alcohol}$, 234 mμ ; ε, 20,000 ; bands at 5.9μ and 6.0μ in the infra-red) can be best represented as (XVII). The corresponding methyl ester (XVIIa, b. p. 135°/0.2 mm., $\lambda_{max}^{alcohol}$, 234 mμ; ε, 14, 000 ; bands at 5.8μ and 6.0μ in the infra-red) was characterised by a semicarbazone, m. p. 214° and a 2 : 4-dinitrophenylhydrazone, m. p. 149-50°. The maxima at 234 mμ in the ultraviolet is due to the combined effect of the two chromophoric systems present in the compound.

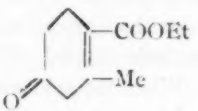
The neutral fraction with a very *strong ketonic smell* could be obtained as a low melting crystalline solid (m.p. 44° ; $\lambda_{max}^{alcohol}$, 296 mμ ; ε, 24, 400). It was characterised by a semicarbazone, m. p. 233° and a 2 : 4-dinitrophenylhydrazone, m. p. 215°. Its structure was proved by reduction with lithium aluminium hydride, followed by dehydrogenation with 10% Pd—C, when 1 : 7-dimethylnaphthalene, identified through its picrate (Barnett and Sanders, *J. Chem. Soc.*, 1933, 437 ; Darzen and Heinz, *Compt. rend.*, 1927, **184**, 33), was obtained. The ketone has therefore been assigned the structure (XV) and is derived from reaction at position-1 to furnish the intermediate (VIII) which undergoes ring-closure between the carbonyl group of the side chain and the β-methyl group on the ring, which is activated by the keto group through the double bond. A somewhat remote possibility that the ketone has the structure (XVI), derived from reaction at the methylene position next to the keto group, is eliminated by synthesis of an authentic specimen of (XVI) and direct comparison with the above ketone. The results from the two foregoing cases definitely establish that the reaction with (V) occurs at the two possible positions and almost equivalent amounts of the two products are obtained.

Ethyl 4-keto-3-methyl-2-furyl-Δ^2-*cyclo*hexene-1-carboxylate (VII) was prepared in the following way. Ethyl 2-furoylacetate (Barger, Robinson and Smith, *J. Chem. Soc.*,

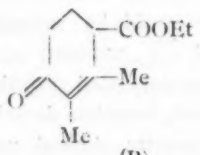
1937, 721) was condensed with vinylmethyl ketone in presence of catalytic amount of sodium ethoxide to yield the aldol (XIX), which on further treatment with sodium ethoxide could be dehydrated to the Hagemann's ester analogue, ethyl 4-keto-2-furyl-Δ^2-*cyclo*hexene-1-carboxylate (VI). Methylation of this in presence of sodium ethoxide furnished the required compound (VII). Both these compounds were characterised by preparation of their solid derivatives. Condensation of (VII) with vinylmethyl ketone under a variety of conditions afforded a thick, yellow, viscous liquid which never solidified. This material had $\lambda_{max}^{alcohol}$, 321 mμ, and nothing around 240 mμ that could be expected if the desired compound (XVIII: R′=Et) was present. Purification by the method worked out in the previous case could not be applied here due to the presence of acid-sensitive grouping (XX) in both the expected isomers. Hydrolysis of the condensation product with 10% KOH was remarkably sluggish, suggesting tertiary character of the ester group. From the resulting gummy product could be isolated only one crystalline acid (m. p. 233° with decomposition ; $\lambda_{max}^{alcohol}$, 323 mμ ; ϵ, 24,000). The analysis agreed with the formula $C_{16}H_{18}O_5$ that corresponded with the structure (X). When the acid was slowly heated at its melting point, complete decarboxylation occurred to furnish a neutral gum which in the infra-red spectra showed very strong bands at 5.84μ and 6.0μ, confirming the presence of saturated and conjugated carbonyl groups in the system. All these observations agree with the structure (X) for this compound. No other acidic material could be isolated and the crude gummy residue, left after removal of the above crystalline acid, also did not show any absorption around 240 mμ region in the ultraviolet. It is somewhat interesting to observe that in the furan derivative reaction occurred exclusively at the 1-position in contrast to the mixture that was obtained in the case of the simpler analogue (V). This specificity suggests that in the transition stage conjugation of the furan ring with the keto group through the double bond is favoured over the *cis*-furacrylic system, and this could be due to the increased resonance stability in the former system. A number of analogous derivatives are now being studied to evaluate this point more thoroughly.

After this work had been completed, a report on the alkylation of ethyl 4-keto-2 : 3-dimethyl-Δ^2-*cyclo*hexene-1-carboxylate (V) was published by Dyer, Kidd and Walker (*J. Chem Soc.*, 1952, 4778). The above authors claimed that in presence of sodium methoxide in dry ether the above compound condensed with *p*-cyanobenzyl bromide to afford exclusively 1-(*p*-cyanobenzyl)-4-keto-2 : 3-dimethyl-Δ^2-*cyclo*hexene-1-carboxylate (XXI). This is contrary to our results. The English workers argued that for Hagemann's ester (IV), *Form* (*A*) would be favoured by hyperconjugation and that this was in line with the fact that the first stage alkylation of Hagemann's ester occurred at the position next to the keto group, viz., position 3. For the dimethyl compound (V), they argued that hyperconjugation would favour the *Form B* as the more stable form and hence alkylation would take place next to the carbethoxyl group, position-1. These arguments are, however, not quite convincing. Moreover, the experiments described in this communication very clearly demonstrate that in contrast to the highly selective alkylation in Hagemann's ester, a mixture of products has always been obtained in the alkylation of methyl Hagemann's ester (V).

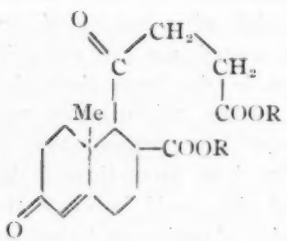
On the basis of their rather fallacious arguments, Walker *et al.* (*loc. cit.*) assigned the structure (XXI) to their product which they thought was formed exclusively. This appears to be rather unlikely, particularly in the light of the present work, unless the alkylation with cyanobenzyl bromides is peculiar by themselves. It is very likely that they were handling a mixture of products derived from alkylation at both the reactive centres rather than a single pure compound of the assigned structure (XXI). In the light of the present work the above conclusion appears to be inescapable, and, in fact, some of the observations recorded by Walker *et al.* can be better accounted for on the basis of the above hypothesis. A careful reinvestigation of their work is highly desirable and will be reported in a subsequent communication. Further work on the chemistry of mesomeric anions derived from compounds of the type (XXII) is being continued.



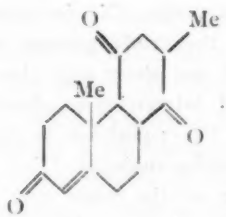
(A)



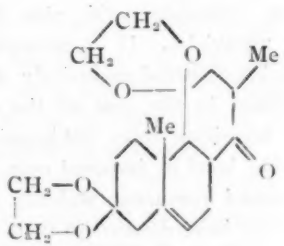
(B)



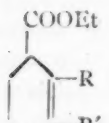
(I)

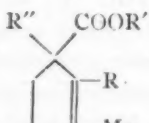


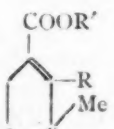
(II)



(III)



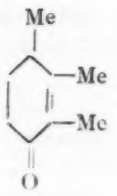




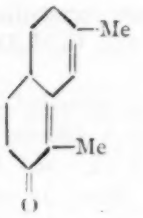
(IV) : R = Me ; R′ = H.
(V) : R = R′ = Me.
(VI) : R = Furyl ; R′ = H.
(VII) : R = Furyl ; R′ = Me.
(XXII) : R = Substituent; R′ = Me.

(VIII) : R = Me , R′ = Et; R″ = γ-keto-butyl.
(IX) : R = Furyl ; R′ = Et; R″ = γ-keto-butyl.
(X) : R = Furyl ; R′ = H; R″ = γ-keto-butyl.

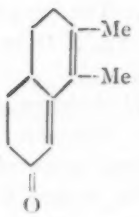
(XI) : R = R″ = Me; R′ = H.
(XIa) : R = R′ = R″ = Me.
(XII) : R = Me ; R′ = Et; R″ = γ-keto-butyl.
(XIII) : R = Furyl ; R′ = Et; R″ = γ-keto-butyl.



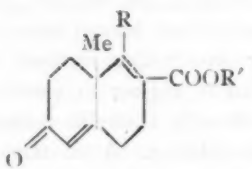
(XIV)



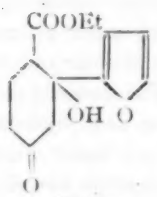
(XV)



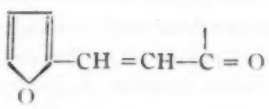
(XVI)



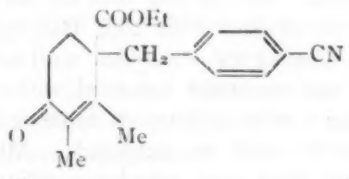
(XVII): R = Me ; R′ = H.
(XVIIa): R = R′ = Me.
(XVIII): R = Furyl ; R′ = H.
(XVIIIa): R = Furyl ; R′ = Me.



(XIX)



(XX)



(XXI)

EXPERIMENTAL

Ethyl 4-Keto-2 : 3-dimethyl-Δ^2-cyclohexene-1-carboxylate (V). — Ethyl 4-keto-2-methylcyclohexene-1-carboxylate, Hagemann's ester (36.4 g.), was added with stirring to an ice-cold solution of sodium ethoxide, prepared from sodium (4.7 g.) and absolute alcohol (150 c. c.). After stirring for about 30 minutes, methyl iodide (30.0 g.) was added all at once. After stirring for 2 hours at this temperature, the solution was gradually heated to its boiling point and gently refluxed for one hour. A fresh addition of methyl iodide (15.0 g.) was made and the reflux continued until the solution was neutral to litmus. Excess of alcohol was then removed under reduced pressure, water added and the oil taken up in ether. After washing the ether extract twice with water, it was dried over anhydrous sodium sulphate, the solvent removed and the residual oil distilled, b. p. 105-106°/2 mm., yield 34 g. The above procedure is a definite improvement over the previous published methods (Bergmann and Weizmann, *J. Org. Chem.*, 1939, **4**, 267 ; Smith and Rouault, *loc. cit.*). The semicarbazone, prepared in the usual way, after one crystallisation from alcohol had m. p. 206°. (Found : C, 57.16 ; H, 7.53. $C_{12}H_{19}O_3N_3$ requires C, 56.91 ; H, 7.51 per

cent). The 2:4-dinitrophenylhydrazone crystallised from alcohol in reddish flakes, m. p. 133°. (Found: C, 54.40; H, 5.34. $C_{17}H_{20}O_6N_4$ requires C, 54.25; H, 5.31 per cent).

Methylation of Ethyl 4-Keto-2:3-dimethyl-Δ^2-cyclohexene-1-carboxylate.—The above keto-ester (15 g.) was added to a solution of potassium *tert.*-butoxide, under nitrogen, prepared from potassium (3.2 g.) and *tert.*-butyl alcohol (100 c. c.). The solution turned deep red and after about 30 minutes the insoluble potassium salt separated. This was then cooled in ice and methyl iodide (12.0 g.) was added and the mixture left overnight under nitrogen, by which time the reaction was almost complete. A further addition of methyl iodide (6.0 g.) was made, the mixture gently refluxed for 2 hours, then concentrated under reduced pressure and poured into water. The precipitated oil was extracted with ether and the ether extract after washing with water was dried and concentrated. The residual oil distilled at 105-107°/1.5 mm. as a colorless mobile oil. The above oil was next hydrolysed with 10% alcoholic potassium hydroxide solution (from KOH, 7.5 g.) under nitrogen for 6 hours. After removing most of the solvent the dirty brown residue was dissolved in water and extracted with ether. On removal of the ether no residue was left.

2 : 3 : 4-*Trimethyl*-Δ^2-cyclo*hexenone* (XIV).—The aqueous alkaline solution from above on being carefully acidified with HCl (dil.) with ice-cooling left a gummy acid. This was taken up in ether. The gummy acid left on removal of the ether was heated in an atmosphere of nitrogen with 10% HCl (50 c. c.), when a vigorous gas evolution started. The heating was continued until no further gas was evolved. After cooling, the solution was repeatedly extracted with ether. The ether extract was then washed several times with portions of dilute sodium bicarbonate solution until no more acidic material could be extracted. After washing finally with water, the ether extract was dried over anhydrous sodium sulphate and the ether carefully removed. The residual oil distilled at 95-98°/16 mm. as colorless oil, yield 4 g. $\lambda_{max}^{alcohol}$, 244 mμ; ϵ, 13200. (Found: C, 78.04; H, 10.18. $C_9H_{14}O$ requires C, 78.26; H, 10.14 per cent).

The *semicarbazone*, prepared in the usual way, crystallised from ethanol in shining needles, m. p. 210°. (Found: C, 61.13; H, 8.64. $C_{10}H_{17}ON_3$ requires C, 78.26; H, 10.14 per cent).

The 2:4-*dinitrophenylhydrazone* was obtained as vermillion-red small needles which after crystallisation from a large volume of alcohol had m.p. 165°. (Found: C, 56.67; H, 5.76. $C_{15}H_{18}O_4N_4$ requires C, 56.60; H, 5.66 per cent).

4-*Keto*-2 : 3 : 3-*trimethyl*-Δ^1-cyclo*hexene*-1-*carboxylic Acid* (XI).—The sodium bicarbonate extract, obtained above, was cooled in ice and carefully acidified with HCl (dil.). A brown gummy acid was precipitated. This was extracted with ether in the usual way, the ether removed and the residual crude acid (8.0 g.) dried. On trituration with a little ethyl acetate the gum solidified. The crystalline acid was filtered and recrystallised twice from ethyl acetate-petrol ether mixture, m.p. 120°. (Found: C, 66.27; H, 7.87. $C_{10}H_{14}O_3$ requires C, 65.93; H, 7.68 per cent). The crude gummy acid left after removal of the crystalline acid was esterified with anhydrous methanol (70 c. c.) and H_2SO_4 (conc., 4 c. c.) for 12 hours. The ester (XIa) was

isolated in the usual way and purified by distillation, b. p. 125-27°/10 mm. (Found : C, 67.53 ; H, 8.08. $C_{11}H_{16}O_3$ requires C, 67.34 ; H, 8.16 per cent).

The *semicarbazone* of the ester, prepared in the usual way, was crystallised twice from very dilute methanol in silky needles, m. p. 143.5°. (Found : C, 57.24 ; H, 7.54. $C_{12}H_{19}O_3N_3$ requires C, 56.91 ; H, 7.5 per cent).

Condensation of Ethyl 4-Keto-2 : 3-dimethyl-Δ^2-cyclohexene-1-carboxylate with Methylvinyl Ketone

A mixture of the keto-ester (39.3 g.) and methylvinyl ketone (15.5 g.) was added to an ice-cold solution of potassium *tert.*-butoxide under nitrogen, prepared from potassium (1.1 g.) and *tert.*-butyl alcohol (80 c.c.), when a deep red solution was obtained which was left overnight at room temperature under nitrogen. It was then acidified with the calculated amount of acetic acid and poured into water. The precipitated heavy oil was isolated by ether extraction and the extract was washed successively with water, 10% sodium carbonate solution and again with water. After drying over anhydrous sodium sulphate, the solvent was removed and the residual oil distilled, when two distinct fractions could be separated : (*a*) b.p. 100°-130°/0.2 mm., 13 g. (*b*) b. p. 140°-160°/0.2 mm., 20 g. There was a high boiling polymeric residue in the distillation flask.

The first fraction on redistillation boiled at 105°-108°/0.15 mm. and was the unchanged keto-ester.

The second fraction on redistillation boiled at 147°-152°/0.15 mm. as a mobile pale yellow liquid. The distillate had $\lambda_{max}^{alcohol}$, 242 mμ (ϵ, 8210) but the maxima was somewhat diffused indicating non-homogeneity.

The above condensation product (29 g.) was hydrolysed by refluxing under nitrogen with KOH (30 g.), water (30 c. c.) and methanol (250 c. c.). The alcohol was then removed under reduced pressure and the residue was dissolved in water. This aqueous solution was then extracted with several portions of ether to remove neutral matter, if any present. But on working up the extract no organic residue was obtained.

2-Keto-1 : 7-dimethyl-$\Delta^{1:9:7}$-hexahydronaphthalene (XV).—The solution from the above operation was then acidified with ice-cooling and the gummy acid extracted with several portions of ether, and the ether distilled off. The residue was then heated under nitrogen with water (300 c.c.) and HCl (conc., 100 c. c.) when a brisk gas evolution started. Heating was continued until this gas evolution was complete, which required about 30 to 40 minutes. After cooling, the aqueous solution was extracted with ether and the ether layer washed several times with small portions of 10% sodium bicarbonate solution until no more acidic matter could be extracted. The neutral ether extract on evaporation afforded a pale yellow mobile oil with a characteristic ketonic smell, which distilled at 114-16°/0.7 mm., as a colorless mobile liquid, yield 8.0 g. This oil on keeping gradually solidified and after two crystallisations from ether-petrol ether mixture had m. p. 44°; $\lambda_{max}^{alcohol}$, 296 mμ ; ϵ, 24, 400. (Found : C, 81.87 ; H, 9.4. $C_{12}H_{16}O$ requires C, 81.8 ; H, 9.09 per cent).

The *semicarbazone*, which formed very readily, was crystallised from a large volume of alcohol, m. p. 233°. (Found : C, 66.86 ; H, 8.13. $C_{13}H_{19}ON_3$ requires C, 66.95; H, 8.15 per cent).

The 2 : 4-*dinitrophenylhydrazone* was obtained as deep red flakes from chloroform-alcohol mixture, m. p. 215°. (Found : C, 60.30 ; H, 5.74. $C_{18}H_{20}O_4N_4$ requires C, 60.67 ; H, 5.61 per cent).

The above ketone was reduced with lithium aluminium hydride and the crude alcohol was dehydrogenated with 10% Pd—C initially at 220° and finally at 280° over a period of about 1½ hours. The reaction product was isolated in the usual way and purified by distilling over metallic sodium. The distillate with a characteristic naphthalene odour instantly formed a picrate which after one crystallisation from alcohol was obtained as lemon-yellow needles, m. p. 120-21°, unaltered by repeated crystallisation. Lit. reports m.p. 120° (Barnett and Sanders, *loc. cit.* Darzens and Heinz, *loc. cit.*). (Found : C, 55.72 ; H, 4.21. Calc. for $C_{18}H_{15}O_7N_3$: C, 56.10 ; H, 3.90 per cent).

6-Keto-1 : 9-dimethyl-$\Delta^{1:5:10}$ *- hexahydronaphthalene-2-carboxylic Acid* (XVII).—The aqueous alkaline solution was acidified with ice-cooling and the gummy precipitate extracted with ether. After washing with two portions of water, it was dried over anhydrous sodium sulphate and the solvent removed. The residual gum (12 g.) slowly crystallised. Direct crystallisation of the crude acid to obtain pure sample was extremely difficult due to contamination of some polymeric material. Hence, it was esterified with methanol and sulphuric acid in the usual way and the ester purified by distillation, b. p. 135°/0.2 mm. $\lambda_{max}^{alcohol}$, 234 mμ ; ε, 14,000. (Found : C, 71.35 ; H, 8.07. $C_{14}H_{18}O_3$ requires C, 71.8 ; H, 7.69 per cent).

The *semicarbazone* was very readily obtained and after one crystallisation from methyl alcohol had m.p. 214°. (Found : C, 61.96 ; H, 7.36. $C_{15}H_{21}O_3N_3$ requires C, 61.93 ; H, 7.21 per cent).

The 2 : 4-*dinitrophenylhydrazone* was crystallised from methyl alcohol-chloroform mixture in orange-red flakes, m. p. 149-50° ; $\lambda_{max}^{alcohol}$, 389 mμ ; ε, 32,400. (Found : C, 58.38 ; H, 5.53. $C_{20}H_{22}O_6N_4$ requires C, 57.97 ; H, 5.31 per cent).

The acid was readily obtained pure by hydrolysis of the above ester with 10% alcoholic KOH, followed by isolation in the usual way. The keto-acid was crystallised from a mixture of ethyl acetate and methanol, m. p. 162°. (Found : C, 70.90 ; H, 7.43. $C_{13}H_{16}O_3$ requires C, 70.91 ; H, 7.27 per cent).

7 - Keto-1 : 2 - dimethyl-$\Delta^{1:8}$*-hexahydronaphthalene* (XVI).—A mixture of 2 : 3-dimethyl*cyclo*hexenone (15 g.) and ethyl formate (18 g.) was added to a suspension of dry sodium methoxide, prepared from sodium (5.5 g.), suspended in anhydrous benzene (150 c. c.) under nitrogen. The whole mixture was cooled in ice during addition. The reaction mixture was left overnight under nitrogen. The resulting cake of sodium salt was then decomposed with water and the benzene layer removed. The alkaline solution was then just acidified with dilute acetic acid and the precipitated oil extracted with ether. On removal of the ether, a brown oil (15 g.) was obtained. This crude formyl ketone (15 g.) and methylvinyl ketone (7.0 g.) in *tert.*-butyl alcohol (25 c. c.) were cooled in ice under nitrogen and a solution of potassium *tert.*-butoxide from potassium (0.6 g.)

in *tert.*-butyl alcohol (25 c. c.) was added. After allowing it to stand overnight, the reaction mixture was poured into water, and extracted with ether. The ether extract was washed with dilute alkali solution and water, and dried. The residual crude condensation product (18 g.), left after removal of the ether, was directly cyclised in the following way.

The crude product (18 g.) in dioxan (375 c. c.) was cooled in ice and to this was added an ice-cold solution of KOH (15 g.) in water (375 c. c.). The addition was done under nitrogen and the mixture was left at room temperature overnight. It was then diluted with water and extracted with several portions of ether. The ether extract was washed with water, dilute acid solution, again with water, and finally dried. The oil remaining after removal of the ether distilled at 110-12°/0.3 mm. as a colorless mobile oil with a characteristic smell. This ketone gradually solidified and after two crystallisations from ether-petroleum ether mixture had m. p. 45.5° . $\lambda_{max}^{alcohol}$, 296 mμ ; ε, 24, 700. (Found : C, 81.4 ; H, 9.12. $C_{12}H_{16}O$ requires C, 81.8 ; H, 9.09 per cent).

The *semicarbazone* was phototropic and gradually turned yellow, m. p. 237°. (Found : C, 67.02 ; H, 8.17. $C_{13}H_{19}ON_3$ requires C, 66.95 ; H, 8.15 per cent).

The 2 : 4-*dinitrophenylhydrazone* was obtained as deep red flakes, m. p. 213.5°. (Found : C, 60.77 ; H, 5.90. $C_{18}H_{20}O_4N_4$ requires C, 60.67; H, 5.61 per cent).

*Ethyl 4-Keto-2-furyl 2-hydroxy*cyclo*hexane-1-carboxylate* (XIX).—A mixture of ethyl 2-furoylacetate (4.6 g.) and methylvinyl ketone (2.0 g.) was added to an ice-cold solution of sodium ethoxide, prepared from sodium (0.06 g.) and absolute alcohol (10.0 c.c.), under nitrogen. The mixture was allowed to warm up to room temperature and left overnight under nitrogen. The resulting solid cake was decomposed with ether and water ; the aqueous layer was extracted twice with ether and the combined ether extract was washed with water, 10% sodium bicarbonate solution, again with water, and finally dried over anhydrous sodium sulphate. The viscous residue, left after removal of the ether, very readily solidified. This was crystallised from a mixture of ether and petroleum ether (b.p. 30°-60°), m.p. 97°, yield 5.1 g. The compound was recrystallised once from the same solvent and was obtained in fine silky needles, m. p. 98°. (Found : C, 61.93 ; H, 6 34. $C_{13}H_{16}O_5$ requires C, 61.9 ; H, 6.35 per cent).

*Ethyl 4-Keto-2-furyl*cyclo*hexene-1-carboxylate* (VI).—*(a)*. The above crystalline aldol (5.0 g.), dissolved in dry benzene (25 c. c.), was added to a solution of sodium ethoxide, prepared from sodium (0.12 g.) and alcohol (20 c. c.). The mixture was left overnight at room temperature under nitrogen. Next day it was refluxed on a steam-bath under nitrogen for 1½ hours. It was then cooled and poured into cold water containing the calculated amount of acetic acid. The organic layer was removed, the aqueous solution was twice extracted with ether and the combined organic extract was then washed with water, 10% sodium bicarbonate solution, again with water, and finally dried over anhydrous sodium sulphate. After removal of the ether, a pale brown viscous oil was left, which distilled at 148°-152°/0.6 mm. as a pale yellow somewhat viscous oil (3.5 g.). This was redistilled and a fraction boiling at 125°/0.1 mm. was collected for analysis. $\lambda_{max}^{alcohol}$, 318 mμ ; ε, 22,500. (Found : C, 67.00 ; H, 6.66. $C_{13}H_{14}O_4$ requires C, 66.67; H, 6.0 per cent).

The 2 : 4-*dinitrophenylhydrazone* was deep red in colour and after crystallisation from alcohol-chloroform mixture had m. p. 138°. (Found : C, 55.25 ; H, 4.38. $C_{19}H_{18}O_7N_4$ requires C, 55.06 ; H, 4.55 per cent).

The *semicarbazone* after crystallisation from alcohol had m. p. 178°. It was phototropic and readily turned yellow. (Found : C, 57.67; H, 5.94. $C_{14}H_{17}O_4N_3$ requires C, 57.72 ; H, 5.84 per cent).

(*b*). While working with larger quantities it was found unnecessary to isolate the intermediate aldol and the following procedure provided satisfactory results. The mixture of β-keto-ester (148 g.) and methylvinyl ketone (68 g.) was added to an ice-cold sodium ethoxide solution (from sodium, 3.2 g. and alcohol, 100 c. c.) under nitrogen. After allowing it to stand at room temperature overnight, a solution of sodium ethoxide from sodium (2.5 g.) and alcohol (200 c. c.) was added, followed by dry benzene (300 c. c.). The whole mixture was refluxed in an atmosphere under nitrogen for about 3 hours, cooled, poured into acidulated water and worked up as before. The product distilled at 158°-162°/1.0 mm., yield 120 g.

Ethyl 4-Keto-3-methyl-2-furyl-Δ^2*-cyclohexene-1-carboxylate* (VII).—The foregoing keto-ester (VI, 21 g.) was added with stirring to an ice-cold solution of sodium ethoxide from sodium (2.1 g.) and absolute alcohol (80 c. c.), kept under nitrogen. A reddish brown solution was obtained. Methyl iodide (28.0 g.) was added and stirring continued at this temperature for 1½ hours. The mixture was then refluxed on the steam-bath for another 2 hours, when the solution became neutral to litmus and only pale yellow in colour. Alcohol was removed under reduced pressure and to the residue water was added and then extracted with ether. The ether extract was then processed in the usual way and evaporated. The residual oil was distilled, b.p. 150-52°/0.7 mm., yield 18 g.

For analytical sample a small portion was redistilled, b. p. 123-25°/0.2 mm. $\lambda_{max}^{alcohol}$, 318 mμ ; ε, 23,450. (Found : C, 67.70 ; H, 6.42. $C_{14}H_{16}O_4$ requires C, 67.73 ; H, 6. 45 per cent).

The 2 : 4-*dinitrophenylhydrazone* was obtained as very dark reddish flakes, m. p. 140°. (Found : C, 55.66; H, 4.67. $C_{20}H_{20}O_7N_4$ requires C, 56.08 ; H, 4.67 per cent).

The *semicarbazone*, which was phototropic, gradually changed to yellow, m.p. 191°. (Found : C, 59.01 ; H, 6.28. $C_{15}H_{19}O_4N_3$ requires C, 59.01 ; H, 6.23 per cent).

*Condensation of Ethyl 4-Keto-3-methyl-2-furyl*cyclo*hexene-1-carboxylate* (VII) *with Methylvinyl Ketone*

A mixture of the ester (20 g.) and methylvinyl ketone (6.5 g.) in dry ether (300 c. c.) was added with efficient stirring to an ice-cold solution of potassium *tert.*-butoxide, prepared from potassium (0.5 g.) and *tert.*-butyl alcohol (60 c. c.), under nitrogen. A purple colour soon developed which gradually turned dark red. After allowing it to stand overnight at room temperature, the dark viscous reaction mixture was poured into water and extracted with ether. The ether extract was washed with 10% sodium bicarbonate solution, several times with water, finally dried and the solvent removed. The residual brown oil was then distilled from a short-path distilling flask. After an initial

forerun of the starting material (10.0 g.), distilling between 140° and 170°/0.2 mm. (bath temp.), a highly viscous oil distilled at 180°-210°/0.2 mm. (bath temp.). This was again redistilled and the major fraction distilling at 180°-190°/0.2 mm. was collected (10 g.). A considerable amount of a high boiling residue was left in the flask. The distillate had $\lambda_{max}^{alcohol}$, 321 mμ; ε, 12,000. In spite of repeated fractionations a purer specimen could not be obtained and the distillate was always contaminated with some non-absorbing material. For the same reason an analytical sample could not be collected and no solid derivative could be prepared. The distillate which was obtained as a pale yellow gum gradually turned brown and after several days completely turned black. Several experiments on the hydrolysis of the above distillate with alkali showed that the ester group was somewhat strongly hindered. The compound (10 g.) was refluxed under nitrogen for 10 hours with a solution, prepared from potassium hydroxide pellets (8.6 g.), water (8.6 c.c.) and methanol (86 c. c.). At the end of this period, the solution was concentrated under reduced pressure and then poured into water. The aqueous solution was extracted three times with ether and after usual processing, the ether was removed leaving a brown gum (7 g.) whose infra-red spectrum was identical with that of the starting material. The alkaline solution was carefully acidified when a dark brown gummy acid precipitated. This was isolated by extracting with ether. The product (3 g.) left after removal of the ether on trituration with dry ether partly solidified. The crystalline acid had m. p. 228-29° (decomp.). The gum remaining after removal of the above crystalline acid resisted all attempts at crystallisation.

The recovered neutral material (6 g.) was again hydrolysed with KOH (3.5 g.), water (3.5 c. c.) and methyl alcohol (35 c. c.). The neutral portion (about 4 g.) was removed in the usual way and the acid was isolated as before. This acidic product (1.5 g.) was relatively pure and completely crystallised. The crude acid had m. p. 229° (decomp.) and after two crystallisations from ethyl acetate and benzene containing some methanol it could be obtained pure as colorless thick needles, m. p. 233° (decomp.). $\lambda_{max}^{alcohol}$, 323 mμ; ε, 21,000. (Found: C, 66.12, 65.84; H, 6.39, 6.19. $C_{16}H_{18}O_5$ requires C, 66.20; H, 6.21 per cent).

Attempts to prepare derivatives of this acid were not successful. Several attempts for the oxidation of this acid with sodium hypobromite and hypoiodide were also unsuccessful. The pure crystalline acid (200 mg.) was slowly heated to its melting point and maintained at that temperature. The crystals melted, followed by gas evolution. After the gas evolution had completely ceased, the residual brown gum was taken up in ether and the extract washed with sodium bicarbonate solution, dried and the ether removed. The remaining brown liquid had sharp bands at 5.84μ and 6.05μ in the infra-red.

The above acid (1 g.) in ether solution was esterified with the calculated amount of diazomethane. The methyl ester obtained, after removal of the unchanged acid by alkali washing and subsequent evaporation of ether, was an almost colorless viscous oil; $\lambda_{max}^{alcohol}$, 321 mμ.

The above crude ester, dissolved in ethyl alcohol (10 c.c.), was added to an ice-cooled solution of sodium borohydride (0.2 g.) in ethyl alcohol (10 c.c.) and left overnight. The reaction mixture was then decomposed with calculated amount of acetic acid and the alcohol removed under reduced pressure. The organic matter was extracted with ether and on removal of the solvent a brown brittle glass was obtained. This had no band at 6.05μ in the infra-red and had $\lambda_{max}^{alcohol}$, 260 mμ.

The author wishes to express his sincere thanks to Prof. Gilbert Stork for his interest and valuable suggestions during the progress of the work as well as for all laboratory facilities.

Department of Chemistry,
Harvard University,
Cambridge, Mass., U.S.A.
and
Department of Chemistry,
Karnatak College,
Dharwar.

Received April 30, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

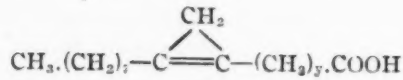
INFRA-RED STUDIES OF STERCULIC ACID AND SOME RELATED COMPOUNDS

By J. P. Verma, Sharda Das Gupta, Bhola Nath and J. S. Aggarwal

Methyl esters of four carboxylic acids related to sterculic acid were synthetically prepared. Their infra-red absorption spectra along with those of sterculic and dihydrosterculic acids were examined. All afforded absorption bands in the 9.9 μ region, characteristic of the *cyclo*propane ring. The presence of bands due to unsaturation in sterculic acid and their absence in the two synthetic *cyclo*propene acids indicate that the constitution of sterculic acid as ω-(2-*n*-octyl*cyclo*prop-1-enyl)-octanoic acid is most probably not correct. The iodine and diene values of sterculic acid and the above compounds also lead to similar conclusions.

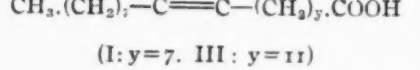
Sterculic acid, the major component of the kernel oil of *Sterculia foetida*, was recently isolated by Nunn (*J. Chem. Soc.*, 1952, 313) and was assigned the constitution ω-{2-*n*-octyl*cyclo*prop-1 enyl}-octanoic acid (I). This being an unusual fatty acid on account of its marked tendency towards polymerisation, further work on its constitution was undertaken.

It is difficult to establish the presence of a *cyclo*propane ring in an organic molecule by ultraviolet absorption spectra or chemical means. Infra-red absorption studies have been solely employed uptil now for the identification of such a ring. *cyclo*Propane itself has been found to absorb at 11.55μ and 9.75μ by Bartleson, Burk and Lankelma (*J. Amer. Chem. Soc.*, 1946, **68**, 2513). Derfer, Pickett and Boord (*ibid.*, 1949, **71**, 2482) from their study of fourteen *cyclo*propane derivatives found that all of them showed strong absorption in the 9.80-10μ region, the band centred at about 9.90μ, ascribed by Herzberg as the symmetric vibration of the *cyclo*propyl ring ("Infra-red and Raman Spectra of Polyatomic Molecules," p. 352, New York, D. Van Nostrand Co., 1945), being a dependable tool for identifying the *cyclo*propane ring. Their results have been confirmed by Marrison (*J. Chem. Soc.*, 1951, 1614), Smith and Rogier (*J. Amer. Chem. Soc.*, 1951, **73**, 3840) and Wiberley and Bunce (*Anal. Chem.*, 1952, **24**, 623). Nunn (*loc. cit.*) has based his structure (I) for sterculic acid mainly on the strong band at 9.8μ in the infra-red spectrum of dihydrosterculic acid, analogous to that in the C_{19}-acid isolated from *Lactobacillus arabinosus* by Hoffmann and Lucas (*J. Amer. Chem. Soc.*, 1950, **72**, 4328). He did not, however, take the infra-red of the sterculic acid itself. In this communication the infra-red studies of sterculic acid and dihydrosterculic acid have been recorded in addition to those of the methyl esters of synthetic ω-{2-*n*-octyl*cyclo*prop-1-enyl}-octanoic acid (I), ω-{2-*n*-octyl*cyclo*propyl}-octanoic acid (II), ω-{2-*n*-octyl*cyclo*prop-1-enyl}-dodecanoic acid (III) and ω-{2-*n*-octyl*cyclo*propyl}-dodecanoic acid (IV). These results show that the structure (I) for sterculic acid is not well founded.



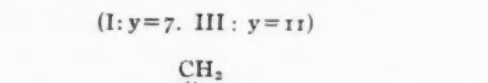
$CH_3.(CH_2)_7—C\overset{CH_2}{=\!=}C—(CH_2)_y.COOH$

(I: y=7. III : y=11)



$CH_3.(CH_2)_7—CH\overset{CH_2}{—}CH—(CH_2)_y.COOH$

((II : y=7. IV: y=11)



$CH_3.(CH_2)_5—CH\overset{CH_2}{—}CH—CH=CH—(CH_2)_7.COOH$

(V)

EXPERIMENTAL

Sterculic Acid.—Nunn (*loc. cit.*) isolated sterculic acid through urea complexes fractionation, but this was not followed as it involved some heating operation to which the acid was found to be especially susceptible. In this laboratory the acid was obtained by low-temperature fractional crystallisation technique from the total fatty acids of the oil (Varma, Nath and Aggarwal, *Oils & Oil-seeds J.*, 1954, 7, No 6, 10), m.p. 19° ; n_D^{35}, 1.4758 ; I.V. (Wijs), 98.2 ; Diene value, 40.3. (Found : C, 77.4 ; H, 11.4. Calc. for $C_{19}H_{34}O_2$: C, 77.5 ; H, 11.56 per cent).

Dihydrosterculic Acid.—Sterculic acid (92.4 mg.) in ethanol in the presence of palladised calcium carbonate (2%) absorbed 7.2 c.c. of hydrogen (nearly one mole.). The solid product after crystallisation from acetone melted at 39-40° ; I. V. (Wijs), 76.5. (Found : C, 76.5 ; H, 12.2. Calc. for $C_{19}H_{36}O_2$: C, 77.0 ; H, 12.16 per cent).

ω-(2-n-*Octyl*cyclo*propyl*)-*octanoic Methyl Ester* (II).—A solution of pure oleic acid (5.g) in anhydrous ethyl ether was treated with excess of diazomethane. The product after removal of the solvent under reduced pressure was dissolved in light petroleum (b.p. 40°-60°) and chromatographed over silica gel with ethyl ether as eluant, yielding the main fraction (2.1 g.), m.p. -1° ; n_D^{40}, 1.4443 ; I.V., 76.5 ; Diene value, 3.2. (Found : C, 77.9 ; H, 12.1. $C_{20}H_{38}O_2$ requires C, 77.4 ; H, 12.3 per cent).

ω-(2-n-*Octyl*cyclo*prop*-1-*enyl*)-*octanoic Methyl Ester* (I).—Stearolic acid (10 g.), prepared by the method of Adkins and Burks ('Org. Syntheses', **27**, p. 76; m.p. 48°), was dissolved in anhydrous ethyl ether, allowed to react with excess of diazomethane and worked up as above, furnishing a product (4.3 g.), m.p. 16° ; n_D^{40}, 1.4489 ; I.V., 80.6 ; Diene value, 5.3. (Found : C, 77.4 ; H, 11.8. $C_{20}H_{36}O_2$ requires C, 77.9 ; H, 11.8 per cent).

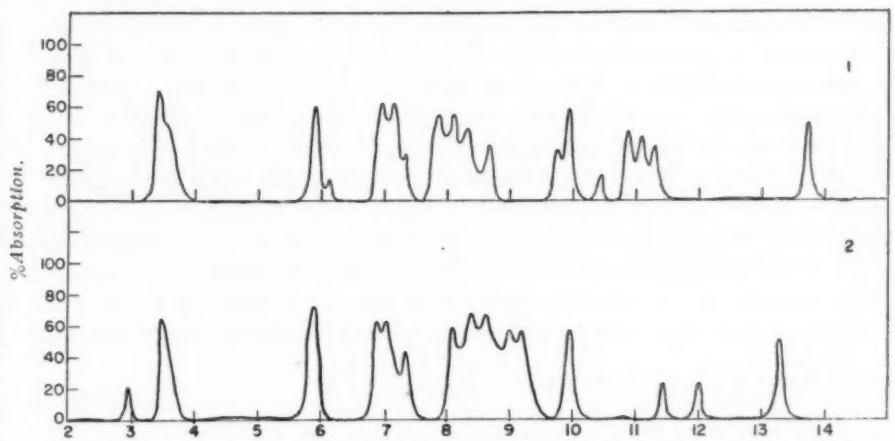
The compound (I) was further purified by distilling at 105°-110°/4 mm. without any sign of decomposition and the distillate exhibited almost the same characteristics as above.

ω-(2-n-*Octylcyclopropyl*)-*dodecanoic Methyl Ester* (IV).—Purified erucic acid (10 g.) was dissolved in anhydrous ethyl ether and treated with excess of diazomethane. The resulting product, after chromatographic separation over silica gel in light petroleum (40°-60°) furnished a main fraction (4.9 g.) melting at -15° ; n_D^{40}, 1.4514 ; I.V., 60.8 ; Diene value, 1.7. (Found : C, 78.3 ; H, 12.4. $C_{24}H_{46}O_2$ requires C, 78.7 ; H, 12.65 per cent).

ω-(2-n-*Octylcycloprop-1-enyl*)-*dodecanoic Methyl Ester* (III).—A solution of behenolic acid (10 g., m.p. 58°) (prepared from erucic acid by a method parallel to that of stearolic acid) in anhydrous ethyl ether was treated with excess of diazomethane, and the product after removal of the solvent was dissolved in light petroleum and chromatographed over silica gel with ethyl ether as eluant, yielding a product (4.1 g.), m.p. 18° ; n_D^{40}, 1.4520 ; I.V., 68.8 ; Diene value, 5.0. (Found : C, 78.6 ; H, 11.9. $C_{24}H_{44}O_2$ requires C, 79.1 ; H, 12.2 per cent).

Infra-red Spectra.—The data recorded were obtained with a Grubb-Parsons spectrometer having a sodium chloride prism. All the above substances were examined in a solution of known concentration in purified carbon tertachloride in the region 2.8μ to 7μ and carbon disulphide in the region 7μ to 15μ in a rock salt cell having a capacity of 0.1 ml.

FIG. 1



Curve 1 refers to sterculic acid and curve 2 to ω-(2-*n*-octyl*cyclo*prop-1-enyl)-octanoic methyl ester.

DISCUSSION

The infra-red absorption spectra of sterculic acid and ω-(2-*n-cyclo*prop-1-enyl)-octanoic methyl ester (I) are shown in Fig. 1 as wave-lengths vs. percentage absorption. Dihydrosterculic acid and the synthetic methyl esters prepared from oleic (II), erucic (IV) and behenolic (III) acids furnised absorption spectra similar to that of ω-(2-*n*-octyl*cyclo*prop-1-enyl)-octanoic acid.

The absorption bands of both the acids and the synthetic acid esters with the exception of the 9.8-10μ are very similar to those of long-chain fatty acids and their esters.

Sterculic acid, dihydrosterculic acid and the four synthetic acid esters (I-IV) all show bands in the 9.8-10μ region, sterculic acid itself absorbing strongly at 9.92μ associated with a weaker band at 9.70μ, and the dihydrosterculic acid and the acid esters showing bands of medium intensity at 9.90μ. Since all the four synthetic methyl esters of the acids (I-IV) have exhibited identical bands in this region, there may be a possibility that the characteristic bands for *cyclo*propane and *cyclo*propene derivatives occupy the same position.

The spectrum of sterculic acid also exhibits bands of nearly medium intensity at 6.09μ and 14.50μ due to unsaturation. These bands vanish on the catalytic hydrogenation of the acid to dihydrosterculic acid and are also absent in the spectra of two synthetic *cyclo*propene acid esters (I and III). The presence of a double bond inside the three-membered carbon ring in sterculic acid, as shown by Nunn (*loc. cit.*), therefore appears doubtful.

Further points against the proposed stucture ascribed by Nunn to sterculic acid are brought out by the facts that the iodine values of both synthetically prepared ω-(2-*n*-octyl*cyclo*prop-1-enyl)-octanoic and -dodecanoic methyl esters (I and III) are somewhat less than one double bond (80.6 and 68.8 as against 81.8 and 69.7 respectively) and they have almost negligible diene values (5.3 and 5.0 respectively.) The iodine value of sterculic acid, however, is more than one double bond (98.2) and it also possesses sufficiently high diene value (40.3). The typical unsaturation of *cyclo*propane ring compounds towards some specific additive reagents has been demonstrated by Kohler and Conant (*J. Amer. Chem. Soc.*, 1917, **39**, 1404). This fact has also been observed in the present study of the iodine values of dihydrosterculic acid and the two synthetic *cyclo*propane compounds (II and IV). The results mentioned above therefore show that the double bond in sterculic acid probably is outside the three-membered carbon ring and not as shown by Nunn (I).

A structure (V) for sterculic acid has already been proposed by Verma, Nath and Aggarwal (*Nature*, 1955, **175**, 84) and further work for its confirmation is in progress.

NATIONAL CHEMICAL LABORATORY OF INDIA,
POONA.

Received June 2, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

STUDIES IN CHROMIUM OXIDE SOLS. PART I. ELECTRICAL CONDUCTIVITY OF CHROMIUM OXIDE SOL

By A.K.M. Trivedi, C. S. Bhatt and A. S. Divatia

Concentrated chromium oxide sols were prepared by adding ammonium carbonate solution to a boiling concentrated solution of chromium chloride. The sols were purified by hot dialysis and the various constituents were analysed. The sols were diluted with water and the electrical conductivity of the diluted sols was determined. It has been found that, (*a*) the specific conductivity of the sol decreases on dialysis, (*b*) the equivalent conductivity of the micelles is much smaller than that of the stabilising electrolyte, if it is present in a free condition, and (*c*) the chromium oxide sol shows the behaviour of a typical colloidal electrolyte.

McBain (*J. Chem. Soc.*, 1919, **115**, 1279) has pointed out that one of the characteristic properties of soaps and similar paraffin chained electrolytes is that at relatively high concentrations, the equivalent conductivity of the micelles increases with increase in concentration. Hartley ("Aqueous Solutions of Paraffin Chain Salts," 1936, p.2; *Trans. Faraday Soc.*, 1938, **34**, 1284; *Kolloid Z.*, 1939, **88**, 22) has suggested that the theory should apply to any inorganic colloidal system in which the particles are charged by the adsorption of ions. This was also found to be true in the case of sulphur sols (Bolam and Trivedi, *Trans. Faraday Soc.*, 1943, **39**, 247) and iron oxide sols (Trivedi, Divatia and Patani, *Proc. Ind. Acad. Sci.*, 1952, **36A**, 530). In the present investigation, it has been pointed out that in the case of well-dialysed chromium oxide sols, the adsorption of ions on the micelles leads to decreased dissociation of the adsorbed ions. Again, the conductivity of the micelles increases with increase in concentration within a certain range, depending upon the purity of the sol. It has also been found that, in general, the charge decreases on dialysis.

Experimental

Chromium oxide sols were prepared after Mittra and Dhar (this *Journal*, 1932, **9**, 315). A concentrated solution of chromium chloride (green variety) was boiled and 14% ammonium carbonate solution was gradually added from a burette with constant stirring until a slight precipitate was formed. The sol, thus prepared, was purified by continuous hot dialysis after Neidle and Barab (*J. Amer. Chem. Soc.*, 1916, **38**, 1962; 1917, **39**, 71). The purified sols were carefully evaporated on a water-bath at 60° till the desired concentration was obtained.

The solid content of the sol was obtained by evaporating the sol in an oven at 120°-130°. Chloride was estimated by Mohr's method, after coagulating the sol with potassium sulphate. The analysis of the sols used for the experiments is shown below.

TABLE I

Sol.	Total solid content (g./litre).	Chloride (g./litre).	Chloride (g.e./litre).	Chromium chloride (g./litre).	Chromium oxide (g./litre).	Purity ratio.
A	60.40	7.021	0.19800	10.450	40 950	7.114
B	42.70	3.333	0.09399	4.962	37.738	11.330

The final column in Table I shows the purity ratio expressed as chromium oxide/chloride.

The electrical conductivity of the sols, diluted to different extents, was measured as before (Trivedi, Divatia and Patani *loc. cit.*) ; 50 ml. of the sol was taken and 50 ml. of water was added. This was termed 0.5C sol. Similarly 0.9C, 0.8C, etc. sols were prepared. The dilution was made with conductivity water (1.5×10^{-6} mhos), the conductivity of water being considered negligible in comparison with the conductivity of the sols, under examination. In each case, several readings of resistances were obtained which differed by less than 0.3%. Table II records the mean values of the resistances.

TABLE II

Conc. of the sols.	Resistance.	Sp. condy. of the micelles.	Equiv. condy. of micelles. (*a*)	Equiv. condy. of free chromium chloride. (*b*)	Ratio *a*/*b*.
		Sol A.			
100%	29.14	7.452×10^{-3}	37.63	91.2	0.412
90	32.56	6.670	37.43	93.0	0.402
80	37.20	5.838	36.85	95.0	0.387
70	43.60	4.980	35.92	98.0	0.366
60	52.20	4.160	35.01	100.0	0.350
50	64.22	3.383	34.18	104.0	0 328
40	83.15	2.611	32.97	108.0	0.305
30	110.76	1.963	33.06	114.0	0.290
20	162.10	1.340	33.84	122.0	0.277
10	267.30	0.812	41.04	135.0	0.304
		Sol B.			
100	64.14	3.386×10^{-3}	36.02	104 8	0.343
90	72.98	2.976	35.18	107.0	0 328
80	83.88	2.589	34.43	109.0	0.315
70	100.05	2.172	33 01	112.0	0 294
60	122.16	1.778	32.54	115 0	0.274
	149 83	1 450	30.86	119.0	0.259
50	196 26	1.107	29 44	123.0	0.239
40	265.36	0.818	29.05	128.0	0 227
30	410.50	0.529	28.16	135.8	0.207
20	524.96	0.413	29.38	141.0	0.208
10	655.03	0.331	35.28	149.0	0.236

DISCUSSION

The specific conductivity (k) of the sol is calculated after calculating the specific conductivity of potassium chloride at 35°, as obtained by plotting the values of the specific conductivity of potassium chloride at different temperatures (Jones and Bardshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780). The chromium oxide sol may contain, besides the gegenions, free NH_4^+ ions, free H^+ ions, free Cr^{3+} ions and free Cl^- ions. The sol was coagulated and the presence of NH_4^+ ions was tested by Nessler's reagent. It was found to be absent. Similarly, the filtrate and the washings after coagulating the sol showed no acidity. The absence of acidity in the case of chromium oxide sol was confirmed by Bassett and Durrant (*J. Chem. Soc.*, 1942, 277) and Yoe and Freyer (*J. Phys. Chem.*, 1926, **30**, 1389). Free Cr^{3+} ions were tested by diphenylcarbazide reagent (Stover, *J. Amer. Chem. Soc.*, 1928, **50**, 2363). A slight pink colour was obtained, indicating that there was only a trace of free Cr^{3+} ions in the sol. Therefore, the well-dialysed sols used in the conductivity experiments contain practically no other electrolytes except the gegenions. Assuming that the conductivity of the sol is due to micelles only, the equivalent conductivity (Λ) of the micelles can be found out by the formula,

$$\Lambda = \frac{1000\ k}{c}$$

where c is the concentration of the chloride in g. ions/litre and k is the specific conductivity of the micelles. The molecular conductivity of chromium chloride, if it is existing in a free condition, is obtained by following the data of Winston and Jones (*Amer. Chem. J.*, 1911, **46**, 396). The equivalent conductivity will be one third the molecular conductivity. Table II shows the equivalent conductivity of the micelles and of chromium chloride, if it was existing in a free condition.

It is found that in all cases the equivalent conductivity of the micelles is much smaller than the conductivity of free chloride, the actual ratio being 20% to 40%. Bjerrum (*Z. physikal. Chem.*, 1924, **110**, 676) studied the osmotic pressure and membrane potential in the case of chromium oxide sol and concluded that about 90% of the chloride ions was adsorbed on the chromium oxide micelles. Rinde (*Phil. Mag.*, 1926, *vii*, **1**, 49) had recalculated Bjerrum's values for membrane potentials and concluded that the true value was somewhat lower, about 75%.

The behaviour of chromium oxide sol is similar to that of sulphur sol (Bolam and Trivedi, *loc. cit.*), iron oxide sol (Trivedi, Divatia and Patani, *loc. cit.*) and stannic oxide sol (Ghosh, *J. Chem. Soc.*, 1929, 2290). Actually, in the case of chromium oxide sol, the degree of dissociation of gegenions comes out to about 25%, which is higher than the corresponding values obtained in the case of sulphur sol, iron oxide sol and stannic oxide sol. The higher value actually obtained (final column in Table II) may be due to the fact that the sol may contain free electrolyte, not allowed for in the calculations. At any rate, it may be concluded that the bulk of the stabilising electrolyte adheres to the micelles.

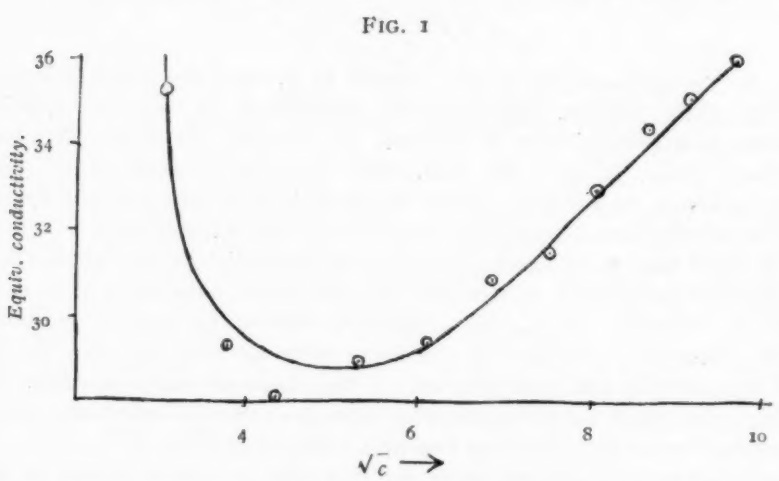
The sol A was dialysed for 20 days, its purity ratio being 7.114. The B sol was dialysed for 35 days, its purity ratio being 11.330. Table III records the conductivity of the same concentration in the case of the sols A and B.

TABLE III

Conc. of the sol (chromium oxide).	Sp. conductivity. Sol A.	Sol B.
10 g./litre	1.20×10^{-3}	0.41×10^{-3}
20	2.19	1.03
30	3.30	2.11
40	4.62	3.12

Thus, in general, the specific conductivity of the sol decreases on dialysis. This is in agreement with Chakravarti and Dhar (*J. Phys. Chem.*, 1926, **30**, 1646) who conclude that as hydrophilic sols are dialysed, the charge decreases. If we compare the variation of the conductivity of the micelles on dilution with the variation of the conductivity of free chromium chloride on dilution, a striking point is noticed. While in the case of free chromium chloride, the equivalent conductivity increases with dilution, in the case of the sol, the conductivity of the micelles first decreases with dilution and then increases with further dilution. This is shown graphically in the case of sol B, where equivalent conductivity is plotted against $\sqrt{c}$. The

FIG. 1



behaviour of chromium oxide sol is in harmony with the behaviour of sulphur sol (Bolam and Trivedi, *loc. cit.*) and iron oxide sol (Trivedi, Divatia, and Patani, *loc. cit.*). The similarity to soap solutions (McBain, *loc. cit.*) is obvious. It may therefore be concluded that the decrease in equivalent conductivity with dilution may take place in any inorganic colloidal system, provided that the conditions are suitable. Hence, such systems may be classified amongst colloidal electrolytes.

The authors' thanks are due to the Ahmedabad Education Society for a generous grant towards chemicals and apparatus.

CHEMISTRY DEPARTMENT,
L.D. ARTS COLLEGE & M.G. SCIENCE INSTITUTE,
AHMEDABAD.

Received July 15, 1954.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

STUDIES IN CARBOHYDRATES. PART III*. INVESTIGATION OF MODAL GUM (*LANNEA GRANDIS*)

V. M. Parikh, T. R. Ingle and B. V. Bhide

Lannea grandis (N. O. Anacardiaceae), commonly known as Modal gum, is found to be a polyuronide, composed of galactose, arabinose and a methyluronic acid in the proportion 5 : 1 : 1. The methyluronic acid is shown to be 4-methylglucuronic acid. The methoxyl content and the uronic anhydride content of the gum indicate that the gum contains only one uronic acid, viz. 4-methylglucuronic acid.

Lannea grandis (N. O. Anacardaceae), commonly known as Modal or Shemat, is a big tree found in deciduous forests of India. Modal gum occurs in the form of tears on the bark of this tree and is initially white in colour, changing to brown afterwards. The gum is used in textile printing and medicinally in asthma and rheumatism. However, practically nothing is known about its composition.

The gum swells in water and dissolves in it on keeping. It is easily soluble in sodium hydroxide. A preliminary purification of the gum was carried out by preparing its aqueous solution and adding it to alcohol, when it was obtained as a white powder (ash, 5.1%). The gum containing 0.64% ash was obtained by treating the gum solution with acidified alcohol. The ash content could not be reduced further by repeating the process.

The purified gum is an acid polysaccharide (equiv. 1245 *ca.*) and is free from nitrogen, sulphur and acetyl group. However, methoxyl group was found to be present in the gum (OMe, 2.38%). It gave positive tests for pentosans and galactan and negative tests for ketoses and methylpentoses. On hydrolysis with 10% sulphuric acid it afforded galactose, arabinose and aldobionic acid. Arabinose and galactose were obtained in the crystalline form from the hydrolysate and were characterised by preparing their functional derivatives.

The uronic acid could not be isolated because of the resistive nature of the aldobionic acid. Drastic hydrolysis of the aldobionic acid furnished galactose only by the decomposition of the uronic acid. The uronic acid could not be identified by simultaneous hydrolysis and oxidation of the gum by HBr and Br_2 according to the method of Goebel and Heidelberger (*J. Biol. Chem.*, 1927, **74**, 613). It was finally proved to be 4-methylglucuronic acid by isolating the aldobionic acid and subjecting it to methanolysis according to White (*J. Amer. Chem. Soc.*, 1948, **70**, 367). The identity of the acid was proved by its different derivatives and their physical constants.

The quantitative analysis of the gum gave ash, 0.64% ; pentosan, 12.31% ; 4-methylglucuronic acid anhydride, 16.32% ; galactan, 71.47% (by difference). No other sugar was detected. The results indicate the proportion of galactan, pentosan and methyluronic acid anhydride as 5 : 1 : 1 respectively.

* The first two papers in this series were published in this *Journal* (1954, **31**, 939, 943).

The methoxyl content of the gum and the uronic acid anhydride content indicate that there should be only one uronic acid, viz., 4-methylglucuronic acid. Smith (*J. Chem. Soc.*, 1951, 2646) on the other hand found both glucuronic and 4-methylglucuronic acid in mesquite gum.

EXPERIMENTAL

The crude gum, supplied by the Forest Department of Bombay State, was a mixture of brown and white gum tears. These, when dissolved in water and precipitated with alcohol, afforded a white powder (ash, 5.1%). The hand-picked, faintly white or colorless gum tears (60 g.) were powdered, suspended in water (200 c. c.) and sodium hydroxide (25 c. c. of 20%) was gradually added to it, when a clear solution was obtained. It was filtered and the filtrate was added to rectified spirit acidified with HCl (800 c.c., 5% HCl) when it was obtained as a white sticky mass. On trituration with absolute alcohol it was obtained as a white powder. Three similar treatments afforded a white powder (ash, 0.64%, mainly Ca^{2+}). The powder did not yield acetic acid on alkaline hydrolysis followed by acidification and steam-distillation.

The gum was acidic to litmus and had equiv. 1245. It was found to contain 2.38% methoxyl. It did not reduce Fehling's solution. It gave positive tests for pentosan and yielded mucic acid (m. p. 215° with decomp.) on oxidation with nitric acid, indicating the presence of galactan or galacturonic acid. Tests for methylpentoses and ketoses were negative. The quantitative analysis of the gum for different constituents has been already given above.

Hydrolysis of the Gum by 10% H_2SO_4.—The purified gum (10 g.) was suspended in 10% H_2SO_4 (100 c. c.) and the mixture was kept overnight. This was necessary, as heating of the suspension caused immediate decomposition of the uronic acid component. After keeping the suspension for 12 to 15 hours, it was heated on a water-bath at 90° and the hydrolysis was followed polarimetrically as well as by estimating the reducing power of the hydrolysate by Bertrand and Mohr's method.

TABLE I

Period (in hours)	0	1	2	3	4	8
$[\alpha]_D^{27}$	could not be observed.	+41°	+67°	+71°	+76°	+76°
Reducing power of the hydrolysate (in terms of glucose)	0	37	72.5	83.3	87	87

The hydrolysate was then neutralised after 8 hours with barium carbonate, filtered and the filtrate was concentrated to a syrup (10 c. c.) under reduced pressure. The syrup was added to absolute alcohol (30 c.c.) when the precipitate of the barium salt of aldobionic acid was obtained. The alcoholic extract was removed from the precipitate of the barium salt (B) and was concentrated to a syrup (A) (6.8 g.).

Examination of the Sugar Syrup (A).—The chromatographic examination of the sugar syrup (A) according to the method of Partridge (*Nature*, 1946, **158**, 270) and developed by the improved method of Novellie (*ibid.*, 1950, **166**, 745) indicated the presence of galactose and arabinose. They were identified by running authentic samples side by

side. The sugar syrup became solid on keeping. It was refluxed with dry methanol (20 c. c.). On cooling, the alcoholic extract was removed and the residue was re-extracted with dry methyl alcohol. The alcoholic extracts were combined and were concentrated to a thin syrup, which yielded crystalline arabinose on keeping in a refrigerator for a couple of days. It was recrystallised according to the method of Anderson *et al.* (*J. Amer. Chem. Soc.*, 1926, **48**, 3172), when pure arabinose was obtained, m. p. 157-58°, $[\alpha]_D^{28}$, + 102° (*c*, 2% in water). Mixed m. p. with an authentic specimen remained unchanged. It afforded diphenylhydrazone, m. p. and mixed m. p., 201°. The chromatographic examination of the residue indicated that the residue was galactose containing traces of arabinose. It was crystallised by following the procedure adopted by Klaas and Sands (*ibid.*, 1929, **51**, 3441), when pure crystalline galactose was obtained, m. p. 164-65°, mixed m. p. with authentic galactose 164-65° ; $[\alpha]_D^{28}$, +80° (*c*, 2% in water). It gave α-methylphenylhydrazone, m. p. and mixed m. p. 186°.

The Barium Salt (B).—The gummy residue (B) was extracted with 90% ethanol till it was chromatographically pure, yield 1.2 g. It contained Ba, 17.55% ; OMe, 7.25 ; $[\alpha]_D^{28}$, + 10° (*c*, 2% in water). Further hydrolysis of this acid by 10% H_2SO_4 was tried, when the hydrolysate turned blackish brown. The neutralised hydrolysate on chromatographic examination indicated the presence of galactose. The uronic acid could not be isolated from the hydrolysate. Attempts were made to oxidise the uronic acid and thus to obtain mucic acid or potassium acid saccharate according to the method of Goebel and Heidelberger (*loc. cit.*), but mucic acid or the acid saccharate could not be isolated.

Methanolysis of the Barium Salt of Aldobionic Acid.—The barium salt (30 g.) was subjected to methanolysis by suspending it in 7% anhydrous methanolic hydrogen chloride and heating it under reflux. The methanolysis was followed polarimetrically, +46°.4 (0 hr.) ; +90°.88 (8 hrs.) ; 92°.8 (16 hrs.) ; +92°.8 (18 hrs.). The solution was then neutralised with silver carbonate, filtered and the filtrate was concentrated under reduced pressure. The syrup, thus obtained, was taken up in acetone (100 c. c.), and anhydrous ether (400 c. c) was added to it when a precipitate was obtained. It was redissolved in acetone (20 c. c.) and precipitated by ether (80 c. c.). The precipitate on distillation under reduced pressure yielded a viscous liquid, yield 3.2 g. $[\alpha]_D^{27}$, 94°.5 (*c*, 2% in MeOH) ; η_D^{27}, 1.4720. [Found : Equiv., 232 ; OMe, 38.95 ; C, 46.18 ; H, 6.78 per cent). Smith (*J. Chem. Soc.*, 1951, 2646) records the following constants for methyl ester of 4-methyl methylglucuronoside : equiv., 240 ; OMe, 38.4% ; $[\alpha]_D^{25}$, +50° (*c*, 2.7% in methanol) ; η_D^{25}, 1.4715 to 1.4737 ; $C_9H_{16}O_7$ requires C, 46.24 ; H, 6.78 ; OMe, 39.4 per cent ; equiv., 236. This indicated that the ester obtained above might be the methyl ester of 4-methyl methylglucuronoside. This was confirmed by preparing its amide by treating the ester with methyl alcoholic ammonia. Crystallisation of the amide from ethanol containing a few drops of water yielded thick white plates, m.p. 234° ; $[\alpha]_{D_{(t)}}^{28}$, +152° (*c*, 1% in water). (Found : C, 43.49 ; H, 6.97 ; OMe, 29.0. Calc. for $C_8H_{15}O_6N$: C, 43.50 ; H, 6.85 ; OMe, 28.05 per cent). Smith (*loc. cit.*) reported m. p. of the amide of 4-methyl methyl-α-*d*-glucuronoside as 235°, $[\alpha]_D^{20}$, +150° (*c*, 1% in water).

MAHARAJA PRATAPSINHA CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE,
POONA-2.

Received July 13, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

DETERMINATION OF THE SOLUBILITY PRODUCT OF NICKEL HYDROXIDE

By P. K. Jena and B. Prasad

Solubility of nickel hydroxide in a number of solutions of hydrochloric acid and in buffer solutions of acetic acid and sodium acetate (1:1) was determined gravimetrically. The p_H of each of the saturated solutions was also measured. From these results the solubility product of nickel hydroxide (K_{sp}) was calculated in both the cases. The most probable value of K_{sp} is considered to be 1.0×10^{-16}.

Britton reported the solubility product of nickel hydroxide to be 8.7×10^{-19}. He used hydrogen electrode in the potentiometric titration of nickel chloride with caustic soda (*J. Chem. Soc.*, 1925, 2110). Gayer and Garrett reported the solubility product of nickel hydroxide as 6.5×10^{-18} (*J. Amer. Chem. Soc.*, 1949, **71**, 2973) from the solubility of nickel hydroxide in hydrochloric acid. Hence, it was considered worthwhile to measure the solubility product afresh.

Experimental

Dry nickel hydroxide was prepared as described earlier (this *Journal*, 1953, **30**, 735). The solubility experiments of nickel hydroxide in HCl were performed in triplicate by continuous shaking at room temperature (24°-26°) for one week which was considered to be enough by preliminary experiments. After shaking, the excess of nickel hydroxide was allowed to settle and the supernatant liquid was filtered through a G_4 glass sintered funnel by applying pressure over the solution. The concentration of the nickel in the solution was gravimetrically determined in duplicate with dimethylglyoxime. The weight of the precipitate in the six determinations did not differ by more than 0.0008 from the mean value. The p_H values of these solutions having the same concentration, measured with a Marconi p_H meter (type T F 511D), did not differ by more the 0.02 from the mean value. The experimental values are recorded in Table I.

Table I

Conc. of HCl (initial).	Conc. of nickel in sat. soln.	f‡.	$a_{Ni^{++}} \times 10^3$.	p_H.	$a_{OH^-} \times 10^5$.	$K_{sp} \times 10^{16}$.
0.0189 g. mol./litre	0.00954 g. mol./litre	0.6033	0.570	7.11	1.301	1.0
0.0757	0.03844	0.4594	1.740	7.07	1.187	2.4
0.1135	0.05772	0.4198	2.382	7.00	1.010	2.4
0.1513	0.07714	0.3967	3.002	6.88	0.766	1.8
0.1892	0.09501	0.3528	3.338	6.80	0.637	1.3

Mean $K_{sp} = 1.8 \times 10^{-16}$.

The concentration of nickel in all the solutions studied was slightly more than half the initial concentration of the acid used. Hence, the possibility of the formation of the basic chloride as a precipitate is ruled out and the presence of some nickel hydroxide in the solution is established.

Another set of solubility of nickel hydroxide was carried out in buffer solutions of acetic acid and sodium acetate (1 : 1). The experimental procedure was the same. The shaking was done at room temperature (28°-30°) for the same period. The results are shown in Table II.

TABLE II

Conc. of acetic acid (initial).	Conc. of nickel in sat. soln.	β.	$f_{\pm}$.	$a_{Ni^{2+}} \times 10^7$.	p_H.	$a_{OH^-} \times 10^7$.	$K_{sp} \times 10^{16}$.
0.040 g. mol./litre	0 020 g. mol./litre	0.675	0.4835	0.653	7.11	1.301	1.1
0.080	0.040	0.550	0 4231	0.931	7.09	1.243	1.4
0 120	0.060	0.470	0.3934	1.110	6.95	0.900	0.9
0.160	0.080	0.415	0.3825	1.272	6.89	0.784	0.8
0.200	0 100	0.375	0.3730	1.398	6.85	0.715	0.7

Mean $K_{sp} = 1.0 \times 10^{-16}$.

DISCUSSION

Solubility in Hydrochloric Acid Solution.—Activity of the hydroxyl ion is calculated from the p_H of the solution taking K_w to be equal to 1.01×10^{-14}. The concentration of the nickel ion in solution is taken to be equal to half the concentration of the acid used, and not the concentration of nickel found experimentally. The amount of nickel in excess of the initial acid is due to the presence of the free nickel hydroxide. The activity coefficient of nickel ion at a particular ionic strength is calculated on the same basis as in an earlier paper (this *Journal*, 1952, **29**, 169). The values of $a_{Ni^{++}}$, a_{OH^-} and K_{sp} for these solutions are shown in Table I.

Solubility in AceticAcid and Sodium Acetate Mixtures.—Nickel acetate dissociates according to the following mechanism (this *Journal*, 1953, **30**, 735):

$$NiAc_2 \xrightleftharpoons{\text{complete}} \underset{(1-\beta)C}{NiAc^+} + \underset{C}{Ac^-}$$

$$\Downarrow$$

$$\underset{\beta C}{Ni^{2+}} + \underset{\beta C}{Ac^-}$$

where C is the molar concentration of nickel acetate and β is the degree of dissociation of $NiAc^+$. According to this mechanism $a_{Ni^{2+}} = \beta C f_{\pm}^2$, where $f_{\pm}^2$ is the activity coefficient of nickel ion. The total acetate ion concentration is $C(3+\beta)$ and a_{Ac^-} (activity of acetate ion) $= C(3+\beta)f_-$, where f_- is the activity coefficient of acetate ion. Assuming the activity coefficient of $NiAc^+$ to be the same as that of Ac^- at the same ionic strength, we have

$$K_2 = \frac{C\beta\,(3+\beta)\,f_{\pm}^2}{(1-\beta)} \qquad \ldots \qquad \ldots \qquad \ldots \quad (1)$$

Knowing the value of K_2 (*loc. cit.*) to be 7.4×10^{-2} and C, the value of β and $f_{\pm}^2$ are calculated by the method of approximation, as in papers reported earlier, till a constant value of β and $f_{\pm}^2$ are found. The activity of nickel ion is calculated from the final value of β and $f_{\pm}^2$. The activity of hydroxyl ion is calculated on the same basis as in the

previous case. The calculated values of $a_{Ni^{2+}}$, a_{OH^-} and K_{sp} for these solutions are shown in Table II.

The absence of agreement in the values of K_{sp} (Table I), calculated from the solubility of nickel hydroxide in HCl, might be due to the incomplete dissociation of nickel chloride. The values of K_{sp}, obtained from buffer solutions of acetic acid and sodium acetate, are more concordant (Table II), and on account of uncertainty in complete dissociation of nickel chloride, the mean of the buffer solution values may be taken to be the correct value.

There is a wide difference between our value and Britton's reported value (*loc. cit.*). Britton used the concentration of nickel and the hydroxide when the first precipitation appeared. Some basic nickel chloride must have come down in the experiments of Britton, because, when insufficient amount of alkali is added to nickel chloride, basic salt is precipitated. Moreover, by oversight Britton took the moles of nickel in solution to be equal to half the moles of alkali added. The calculated solubility product of nickel hydroxide in his experiments, except at the initial stage of precipitation, should be the same throughout. Table III records recalculated values of solubility product in Britton's experiment. The values of the solubility product, except in the beginning when the precipitation begins and towards the end when the precipitation is getting completed, are nearly the same as our values.

TABLE III

Britton's experiment.

Alkali added	p_H.	p_{OH}.	Recalculated value of g. moles of nickel ion per litre of soln.	Recalculated value of solubility product of nickel hydroxide (K_{sp}).
* 0.8 c.c.	6.82	7.32	2.412×10^{-2}	5.6×10^{-17}
10.0	7.00	7.14	1.833×10^{-2}	1.3×10^{-16}
15.0	7.07	7.07	1.543×10^{-2}	1.1×10^{-16}
30.0	7.42	6.72	8.455×10^{-3}	3.1×10^{-16}
40.0	7.75	6.39	4.043×10^{-3}	6.8×10^{-16}
43.5	9.80	4.34	1.466×10^{-3}	3.1×10^{-12}

* Precipitation begins.

Like us, Gayer and Garrett also determined the solubility product of the hydroxide by dissolving nickel hydroxide in hydrochloric acid solutions (*loc. cit.*). Our solubility values agree with Gayer and Garrett's values. Our p_H values agree with Britton's values which were measured with hydrogen electrode. Our K_{sp} values also are of the same order as the corrected values of Britton, but the value of Gayer and Garrett is much lower. There appears to be some error in the measurement of the p_H values of Gayer and Garrett (*loc.cit.*).

Considering Britton's measurements and our measurements, we think that the most appropriate value of K_{sp} for nickel hydroxide would be 1.0×10^{-16}.

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE CUTTACK-3.

Received August 9, 1954.

[Jour. Indian Chem Soc., Vol. 33, No. 2, 1956]

STUDIES IN CARBOHYDRATES. PART IV. INVESTIGATION OF MODAL GUM (*LANNEA GRANDIS*). STRUCTURE OF THE ALDOBIONIC ACID

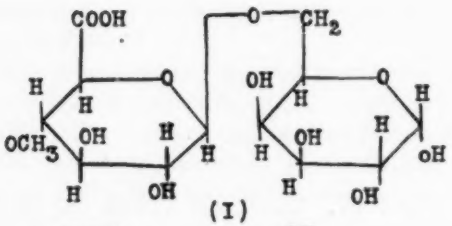
By V. M. Parikh, T. R. Ingle and B. V. Bhide

The structure assigned to the aldobionic acid obtained from Modal gum (*Lannea grandis*) as 4-methyl-1 :6-glucuronosido-galactose has been confirmed by preparing the amide (V) of its fully methylated derivative (III).

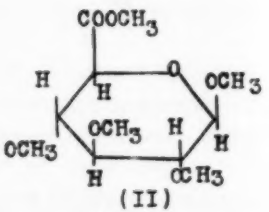
In Part III (this *Journal*, 1956, **33**, 119) it was shown that modal gum gave on hydrolysis an aldobionic acid consisting of one galactose and one methylglucuronic acid unit. A considerable decomposition was, however, observed during the hydrolysis with 10% H_2SO_4, thus resulting in poor yields of aldobionic acid. Hydrolysis with 3% H_2SO_4 afforded a mixture of barium salts of uronic acids. The mixture had Ba, 13.3% and $\alpha_D^{28} \pm 0°$. Barium salt of monouronic acid requires Ba, 26.2%, that of aldobionic acid, 15.66% and of aldotrionic acid, 11.2%. This mixture of the barium salts was subjected to further study.

Methylation of the barium salts of the acids, first with dimethyl sulphate and sodium hydroxide and finally with Purdie's reagent, furnished a product which on distillation under reduced pressure afforded two fractions, A and B. Fraction A was found to be methyl ester of 2 : 3 : 4-trimethyl methylglucuronoside (II), which was confirmed by preparing its amide (m.p. 185°) and comparing its physical properties with the amide of 2: 3: 4-trimethylglucuronic acid, reported by Smith and Cunnen (*J. Chem. Soc.*, 1948, 1141). Fraction B on hydrolysis with aqueous 7% HCl and working out in the usual manner yielded two sugars. The non-acidic reducing sugar was found to be 2 : 3: 4-trimethylgalactose from its physical constants as well as by preparing its anilide, which had m.p. and mixed m.p. with an authentic specimen, 165°. The acidic sugar obtained was shown to be 2 : 3: 4-trimethylglucuronic acid by preparing its crystalline 2 : 3: 4-trimethylglucosaccharo-1: 5-lactone-6-methyl ester (IX), m. p. and mixed m.p. with the authentic sample, 108-109°. The above results indicate that the aldobionic acid present in the modal gum has the structure (I).

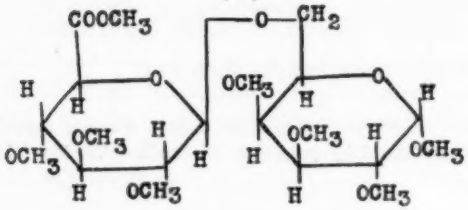
The structure (I) assigned to the aldobionic acid was confirmed by preparing the amide (V) of its fully methylated derivative (III), m.p. 196° ; $[\alpha]_D^{28} - 24°$ (*c*, 0.25% in water). The fully methylated derivative (III) as well as its amide (V) has been described in the literature (Smith and Jackson, *J. Chem. Soc.*, 1910, 74) and the physical constants of both these derivatives agree well with the derivatives obtained in this work.



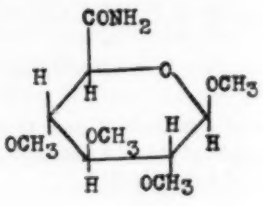
(I)



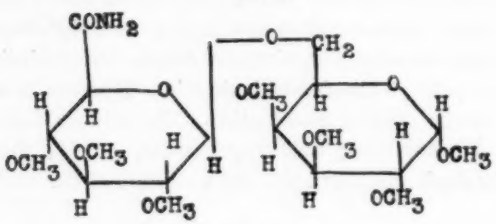
(II)



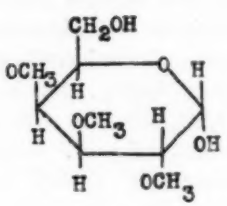
(III)



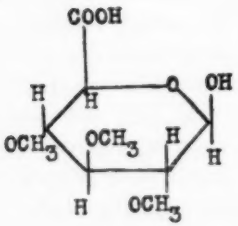
(IV)



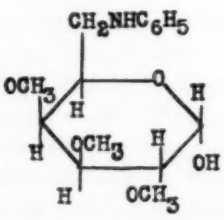
(V)



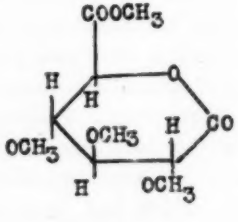
(VI)



(VII)



(VIII)



(IX)

Experimental

Isolation of the Uronic Acids.—The gum (350 g.) was suspended in 3% H_2SO_4 (10 litres) and the mixture was heated at 90° for 10 hours, initially keeping it overnight at room temperature. The solution was neutralised with barium carbonate, filtered and the filtrate was concentrated to a thick syrup (200 c.c.). On pouring this syrup into 90% ethanol (1 litre) a mixture of the barium salts of the uronic acids precipitated. It was separated from the non-acidic reducing sugars by extracting it several

times with boiling alcohol till chromatographically free from sugars. The mixture of the barium salts was a pale yellow amorphous powder, yield 75 g., Ba, 13.3% ; $[\alpha]_D^{28} \pm 0°$.

Methylation of the Mixture of the Barium Salts of the Uronic Acids.—A portion of the barium salts (50 g.) was dissolved in water (150 c.c.), and acetone (100 c.c.) was added until a slight turbidity was observed. The solution was then treated with dimethyl sulphate (525 g.) and sodium hydroxide (950 c.c., 30%). Half of the reagents was added at the room temperature during 4 hours with vigorous stirring till the solution became non-reducing, while the remaining reagents were added at 70° during a period of 7 hours. The faintly alkaline solution was concentrated on a water-bath to a small bulk (250 c.c.), filtered to remove sodium sulphate, and remethylated by using dimethyl sulphate (500 g.) and sodium hydroxide (750 c.c., 30%). After three more methylations the mixture was cooled to 0° and was acidified with 25% H_2SO_4. Sodium sulphate, thus separated, was removed by filtration and the filtrate was extracted with chloroform (200 c.c. each time) three times. Sodium sulphate was also extracted with methyl alcohol, methyl alcohol was removed under reduced pressure and the solid obtained was extracted with chloroform. The extracts of chloroform were combined, washed with water, dried over anhydrous sodium sulphate and the solvent removed, when a mixture consisting of partially methylated uronic acids was obtained in the form of a syrup, yield 38 g., OMe, 35.66%.

The syrup (38 g.) was dissolved in methyl iodide (150 c.c.) and freshly prepared dry silver oxide (50 g.) was added to the refluxing solution with vigorous stirring during 8 hours. Silver oxide was then extracted with dry ether several times. On removal of ether and methyl iodide, the syrup obtained had OMe, 49.5%, yield 30 g. The syrup on remethylation by the above method did not show any rise in its methoxyl content. It was therefore distilled under reduced pressure and the following fractions were obtained. Fraction A : 14.2 g., b.p. 110°-115°/3 mm. Fraction B: 14.2 g., b.p. 268°-280°/3 mm. and the residue 13.0 g. The residue was not distillable and therefore was not examined.

Fraction A.—It is a yellow mobile liquid ; η_D^{28} 1.44880 ; $[\alpha]_D^{28}$ + 31° (*c*, 2.7% in water). (Found : C, 49.78 ; H, 7.4 ; OMe, 57.8. Calc. for $C_{11}H_{20}O_7$: C, 50.0 ; H, 7.57 ; OMe, 58.8 per cent).

The constants reported by Hirst and Jones (*J. Chem. Soc.*, 1938, 1174) for methyl ester of 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside (II) are : η_D^{21} 1.4471 ; $[\alpha]_D^{21}$ + 31° (*c*, 0.7% in water). On treatment with ammonia at 0° for 48 hours, it furnished an amide (IV) which crystallised from ethanol-ether-petroleum ether (40°-60°), m.p. 185°; $[\alpha]_D^{27}$ + 140° (*c*, 1% in water). (Found : N, 5.66 ; OMe, 48.9. Calc for $C_{10}H_{19}O_6N$: N, 5.60 ; OMe, 49.80 per cent). Physical constants reported by Cunnen and Smith (*J. Chem. Soc.*, 1948, 1141) for the amide of 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside (IV) are : m.p. 185° ; $[\alpha]_D^{27}$ + 137° (*c*, 0.7% in water).

Fraction B.—It is a thick pale yellow liquid ; η_D^{27} 1.4684 ; $[\alpha]_D^{27}$ + 24° (*c*, 2% in water). (Found : C, 51.42; H, 7.90 ; OMe, 51.9 ; equiv., 464.1. Calc. for $C_{29}H_{56}O_{12}$: C, 51.29 ; H, 7.69 ; OMe, 51.0 per cent. Equiv., 468). The syrup on keeping for

several days at room temperature deposited white crystals of the methyl ester of hexamethyl-6-glucuronosido-β-methylgalactoside, which were isolated according to the method of Challinor, Hirst and Haworth (*J. Chem. Soc.*, 1931, 258), m.p. 81° ; OMe, 52.2%.

Hydrolysis of Methyl Heptamethylaldobionate (III).—Fraction B (6 g.) was dissolved in 7% aqueous HCl (100 c.c.) and was heated at 90° for 4 hours. The following changes in the optical rotation were observed : + 23°.86 (0 hr.), + 50° (1 hr.), + 60°.66 (2 hours), + 63°.3 (3 hours), +65°.1 (4 hours, and remained constant further). Neutralisation of the hydrolysate with barium carbonate, followed by filtration and concentration under reduced pressure at 40°, furnished a pale yellow powder.

Isolation and Identification of 2 : 3 : 4-*Trimethylgalactose* (VI).—The brown-yellow powder was extracted with dry ether in a soxhlet. The extract on removal of the ether afforded a pale yellow reducing syrup, yield 2.2 g. $\eta_D^{32.7}$ 1.4734 ; $[\alpha]_D^{32.8}$ + 83° (*c*, 0.5% in water). (Found : C, 48.72 ; H, 7.18 ; OMe, 42.2. Calc. for $C_9H_{18}O_6$: C, 48.64 ; H, 8.11 ; OMe, 41.88 per cent). The sugar was identified as 2 : 3 : 4-trimethylgalactose by examining it on a paper chromatogram using butanol and petroleum ether (60°-80°) (30 : 70 v/v) and running authentic sample of 2 : 3 : 4-trimethylgalactose side by side. The anilide of this sugar crystallised from ethyl alcohol, m.p. 165°. (Found : N, 4.87 ; OMe, 31.37. Calc. for $C_{15}H_{23}O_5N$: N, 4.70 ; OMe, 31.3 per cent). This did not depress the m.p. of the authentic specimen of the anilide of 2 : 3 : 4-trimethylgalactose, prepared by the method of McCreath and Smith (*J. Chem. Soc.*, 1939, 387).

Identification of 2 : 3 : 4-*Trimethylglucuronic Acid*.—The residue after ether extraction was extracted with dry chloroform from which the barium salt was precipitated by dry ether as a chromatographically pure, dry, brown powder, yield 3.8 g. [Found : OMe, 30.52 ; Ba, 22.2. Calc. for $(C_9H_{15}O_7)_2Ba$: OMe, 30.65 ; Ba, 22.57 per cent].

The barium salt (2 g.) was dissolved in water (15 c.c.) and bromine (3 c.c.) was added to it. The mixture was kept at room temperature for 4 days ; bromine was then removed by aeration, and the solution was neutralised by barium carbonate, filtered and concentrated under reduced pressure to dryness. It was then boiled with methyl alcoholic hydrogen chloride (3%, 30 c.c.) for 6 hours. The hydrochloric acid was neutralised by silver carbonate and the filtrate was concentrated under reduced pressure and was finally distilled. The syrupy liquid (1 g.) solidified, which was crystallised from ether-petroleum ether mixture, m.p. 108-109° ; $[\alpha]_D^{32.7}$ + 90° (*c*, 1% in water). This did not depress the m.p. of the authentic specimen of the lactone prepared by the method of Smith *et al.* (*J. Chem. Soc.*, 1939, 1734).

Preparation of the Amide of Hexamethyl 6-d-*Glucuronosido-methylgalactopyranoside* (V).—Fraction B (0.5 g.) was treated with anhydrous alcoholic ammonia for 48 hours at 0°. Removal of the solvent furnished white crystals which on recrystallisation from acetone-ether melted at 196° ; $[\alpha]_D^{32.7}$ −24° (*c*, 0.25% in water). (Found : C, 50.51 ; H, 7.8 ; OMe, 46.6. Calc. for $C_{19}H_{35}O_{11}N$: C, 50.32 ; H, 7.7 ; OMe, 47.9 per cent). Jackson and Smith (*loc. cit.*) reported the m.p. of the amide as 196°.

MAHARAJA PRATAPSINHA CHEMICAL LABORATORY,
SIR PARASHURAMBHAU COLLEGE,
POONA-2.

Received July 13, 1955

[Jour. Indian Chem. Soc., Vol. 33, No 2, 1956]

STUDIES IN FRIEDEL-CRAFTS' ACYLATION. PART I. FRIEDEL-CRAFTS' ACETYLATION OF ACETANILIDE AND ACETO-*o*-TOLUIDIDE

By (Miss) M. J. Sacha and S. R. Patel

Friede.-Crafts' acetylation of acetanilide and aceto-*o*-toluidide has been investigated using acetyl chloride. Acetanilide yielded *p*-acetaminoacetophenone, and aceto-*o*-toluidide, 3-acetamino-4-methyl-acetophenone (I). The constitution assigned to (I) has been confirmed by unambiguous synthesis.

Kunckell *et al.* (*Ber.*, 1900, **33**, 2641; 1907, **40**, 3394; 1901, **34**, 124) studied Friedel-Crafts' acylation of acetanilide and its derivatives using various acyl chlorides in presence of excess of anhydrous aluminium chloride and carbon disulphide as the solvent. They found that for the reaction to succeed, it was essential that the acyl halide should have boiling point exceeding 90° or that it should be halogenated. For instance, they reported that, in case of acetanilide, Friedel-Crafts' acetylation failed with acetyl chloride but furnished satisfactory results with acetyl bromide or chloroacetyl chloride. They did not investigate Friedel-Crafts' acetylation of any other acetanilide derivative.

We have, however, successfully carried out the Friedel-Crafts acetylation of acetanilide and aceto-*o*-toluidide using acetyl chloride as the acetylating agent. By investigating the reaction with different proportions of the components at 100° and in the absence of any solvent, it has been established that the acetaminoketone is obtained in good yield on using 1 : 1 : 3 parts by weight respectively of acetanilide (or aceto-*o*-toluidine), acetyl chloride and anhydrous aluminium chloride.

The constitution assigned to the acetaminoketone, obtained from aceto-*o*-toluidide, viz., 3-acetamino-4-methylacetophenone (I), has been confirmed by unambiguous synthesis in the following manner. *p*-Methylacetophenone on nitration afforded 3-nitro-4-methylacetophenone from which, on reduction with iron powder and acetic acid and subsequent N-acetylation with acetic anhydride, 3-acetamino-4-methylacetophenone was obtained, identical with the above product (I).

On oxidation with aqueous potassium permanganate, (I) furnished 3-acetamino-4-methylbenzoic acid, m.p. 267-70° (decomp.), which agreed with the melting point reported in literature for the same acid (Kunckell, *Chem. Zentrl.*, 1912, I, 136).

Experimental

Acetylation of Acetanilide to p-*Acetaminoacetophenone.*—To a cooled mixture of acetanilide (10 g.) and $AlCl_3$ (anhydrous, 30 g.) acetyl chloride (10 g.) was added in small lots with occasional stirring. It was left at room temperature for half an hour and then heated on a water-bath for 3 hours, cooled and decomposed with ice and HCl. The product was filtered and washed with water. It crystallised from boiling water in small plates, m.p. 166-67°, yield 2.5 g. Kunckell (*loc.cit.*, 1900) records the same melting point.

Acetylation of Aceto-o-toluidide to 3-Acetamino-4-methylacetophenone (I).—This reaction was similarly carried out. 3-Acetamino-4-methylacetophenone crystallised from boiling water in white shining plates, m.p. 141-42°, yield 6 g. (Found: N, 7.6. $C_{11}H_{13}O_2N$ requires N, 7.3 per cent).

3-Amino-4-methylacetophenone.—The above acetaminoketone (I) was hydrolysed at 100° with excess of dilute HCl and the product crystallised from petroleum ether in yellowish small needles, m.p. 83-84°. (Found: N, 9.7. $C_9H_{11}ON$ requires N, 9.4 per cent).

The *oxime* of the aminoketone crystallised from dilute alcohol in thin long needles, m.p. 152-53°. (Found: N, 17.3. $C_9H_{12}ON_2$ requires N, 17.1 per cent).

The *N-benzoyl derivative* was prepared by heating the above aminoketone with a slight excess of benzoyl chloride in presence of dilute alkali. It crystallised from boiling water in white shining thin needles, m.p. 124-25°. (Found: N, 5.67. $C_{16}H_{15}O_2N$ requires N, 5.5 per cent).

Reduction of 3-Nitro-4-methylacetophenone: Formation of 3-Amino-4-methylacetophenone.—The suspension of 3-nitro-4-methylacetophenone (5 g.) (Errera, *Gazzetta*, 1891, **21**, 92) in hot water (10 c.c.) was added in small portions to a well-stirred mixture of iron filings (7.5 g.), water (30 c.c.) and acetic acid (2 c.c.) at about 80°, and heating was then continued for half an hour, and the hot solution was filtered immediately. From the filtrate, 3-amino-4-methylacetophenone separated out on cooling. It crystallised from petroleum ether in yellowish small needles, m.p. 83-84°. It did not depress the melting point of the amino-ketone, described above.

N-Acetylation of 3-Amino-4-methylacetophenone: Formation of 3-Acetamino-4-methylacetophenone.—The above mentioned amino-ketone (2 g.) was heated on a water-bath with acetic anhydride (3 c.c.) for half an hour and poured in cold water. The white solid which separated after about half an hour was collected and crystallised from hot water in white shining plates, m.p. 141-42°. It did not depress the melting point of (I), described above.

3-Acetamino-4-methylbenzoic Acid.—3-Acetamino-4-methylacetophenone (2 g.) was heated on a water-bath with a 5% solution of potassium permanganate (120 c.c.) till oxidation was complete. The solution was filtered hot and the filtrate was evaporated on a water-bath to half its bulk. On acidifying it 3-acetamino-4-methylbenzoic acid separated out. It crystallised from boiling water in white small needles, m.p. 267-70° (decomp.). Kunckell (*loc. cit.*) records the same melting point. (Found: Equiv. 191.2. Calc for $C_{10}H_{11}O_3N$: Equiv., 193.0).

M. R. Science Institute,
Gujarat College,
Ahmedabad.

Received January 1, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

MICRO-METHOD FOR ESTIMATION OF NICOTINE GROUP OF ALKALOIDS IN TOBACCO PLANTS

By B. C. Bose, H. N. De and I. H. Dalal

A new micro-method, based on the cyanogen bromide and aniline colour reaction, has been developed for the estimation of nicotine and other pyridine alkaloids in the distillate of tobacco leaves. By this method 2μ g. of nicotine per c.c. could be easily estimated by using a photo-electric colorimeter.

The recovery of nicotine was estimated to be 96 to 98%. For complete recovery of nicotine from a small quantity of leaves etc., a minimum of 300 c c. of distillate requires to be collected.

In literature various methods, such as titration method, silicotungstic acid method etc., have been prescribed for estimation of nicotine group of alkaloids in tobacco plants ("Chemists' Year Book," 1951, p. 1171; "Official Methods of Analysis of A.O.A.C.," 7th Edition, 1950, p. 69). Since these methods require about 2.5-10 g. of tobacco leaves for estimation of these alkaloids, they are not suitable for micro-estimation of nicotine alkaloids needed for the study of the biogenesis of these alkaloids by culture work *in vitro* with leaf, stem and root slices. It is therefore felt necessary to devise a suitable micro-method by which a few mg. of leaves, stems or roots could be used for estimating the nicotine content. The present paper embodies an account of such a method based on photocolorimetric estimation.

Koenig (*J. parkt. Chem.*, 1904, **69**, 105; 1905, **70**, 19) obtained a coloured compound by reacting pyridine nucleus with cyanogen bromide and a primary or a secondary amine. On the basis of this colour reaction an accurate method for estimation of nicotinic acid and its different derivatives had been developed by Swaminathan (*Indian J. Med. Res.*, 1942, **30**, 397; Melnick, *Cereal Chem.*, 1942, **19**, 553) and other workers by using cyanogen bromide and aniline. It was therefore considered desirable to explore the possibility of utilisation of the above cynogen bromide and aniline method also for the micro-estimation of nicotine group of alkaloids in different parts of tobacco plants.

Experimental

Comparative Study of Nicotine Content of dry Tobacco Leaves by Titration and the New Micro-method

Two sets of experiments were first arranged to assess the suitability of this method for nicotine estimations. In one set the nicotine was distilled off from 2.5 g. of tobacco leaves mixed with 25 c.c. of 1% NaOH solution and the nicotine content of the distillate was collected in 5 c.c. of $N/10$-H_2SO_4, and estimated by back titration against $N/10$-NaOH. In another set the distillate was collected in 5 c.c. of 1:1 HCl and the nicotine content was determined by using cyanogen bromide and aniline colour reaction in the following way.

To 1 c.c. of the distillate were added 1 c.c. of 50% sodium acetate buffer, adjusted to p_H 7, 2 c.c. of 2% aqueous aniline solution (aniline freshly prepared), followed by 12 c.c. of cyanogen bromide solution. These were mixed well and allowed to stand for 10 minutes, during which period the maximum intensity of colour was obtained. This colour was then matched against a standard prepared in the same way by taking 1 c.c. solution containing 100 to 150 μg. of nicotine. As the colour was very intense, the visual colorimeter could be used for comparison.

The results of estimation by titration and the present colorimetric method, as presented in Table I, show that percentage of nicotine alkaloids estimated by these methods compares favourably.

TABLE I

[Figures represent the average of six estimations in each batch].

Batch No.	Tobacco leaves taken.	Distillate collected over acid.	Method of estimation.	% Nicotine estimated.
A	2.5 g.	500 c.c. in 5 c.c. of N/10 H_2SO_4	Titration	3.2
B	2.5	500 c.c. in 1 c.c. of 1 : 1 HCl	Visual colorimetric	3.0

Less amounts of leaves (40 mg. to 500 mg.) were then taken and the nicotine content of the distillates (total volume 500 c.c.) estimated colorimetrically by using Klett-Summerson photoelectric colorimeter.

TABLE II

Values of nicotine in small amount of tobacco leaves estimated by photoelectric colorimeter.

[The values represent averages of six sets of experiments in each batch].

Batch No.	Tobacco leaves taken.	Conc. of nicotine standard per c c.	% Nicotine found.
A	500 mg.	20-40 μg.	3.06
B	200	5-10	2.96
C	40	2-4	3 0

The results presented in Table II show that by this new method 2 to 2.5 μg. of nicotine per c.c. of distillate collected from 40 mg. of leaves could be easily estimated by using photoelectric colorimeter. For lower concentrations below 2 μg. per c.c., the intensity of the colour developed was too faint to obtain a wider range of deflection in the scale of the galvanometer. Addition of 2 mg. of nicotine to both the standard and the unknown solutions intensified the colour, and by this "intensification" process nicotine content even below 2 μg. per c.c. could be easily estimated. If a Multiflex galvanometer (B Lange type) is available in hand then this intensification process is not necessary and the faint colour developed by nicotine below 2 μg. will afford a large deflection in 1 : 100 scale of the galvanometer.

Recovery of Added Nicotine

Further accuracy of the method was tested by determining the percentage recovery of nicotine added along with tobacco leaves and distilled off in the usual way. In batch A only 1 mg. of nicotine was distilled and the percentage recovery of nicotine evaluated. In batch B, 1 mg. of nicotine added along with 40 mg. of leaf sample was distilled and the total recovery of nicotine estimated. The total recovery less 1.2 mg. (nicotine content of 40 mg. leaf sample) gave the recovery of 1 mg. added nicotine. From the results of Table III it would appear that 96 to 98% recovery of the added nicotine (1 mg. along with 40 mg. leaf samples) could be assessed by this method.

TABLE III

Recovery of added nicotine by cyanogen bromide method.

[The values represent the average of six experiments in each batch].

Batch No.	Tobacco leaves taken.	Nicotine added.	Recovery of total nicotine.	Recovery of added nicotine.	% Recovery of added nicotine.
A.	Nil	1 mg.	0.98 mg.	0.98 mg.	98
B.	40 mg. containing 1.2 mg. of nicotine.	1	2.16	0.96	96

Minimum Distillate to be collected.—In all the previous experiments 500 c.c. distillate was collected to ensure complete distillation of nicotine. In view of the long time required for the collection of such a large volume of distillate some experiments were made to assess the minimum amount of distillate to be collected for maximum recovery of nicotine. Samples of 1 mg. nicotine, 40 mg. leaves, and 40 mg. leaves plus 1 mg. nicotine were subjected to steam-distillation as before and the distillates were collected to different volumes ranging from 100 to 500 c.c. The results are presented in Table IV.

TABLE IV

% Recovery of nicotine in different volumes of distillates.

[The figures for each batch represent the average of three estimations].

Bach No.	Tobacco leaves taken.	Amount of extra nicotine added	Distillate collected.	Total recovery of nicotine.	% Nicotine recovered.
A	40 mg. of tobacco leaves containing 1.2 mg. of nicotine.	Nil	200 c c.	0 94 mg.	72
B	Do	...	300	1.18	98
C	Do	...	400	1.14	95
D	Do	...	500	1.18	98
E	Do	1 mg.	200	1.43	65
F	Do	,,	300	2.16	98
G	Do	,,	400	2.14	97
H	Do	,,	500	2.16	98
I	Nil	,,	200	0.62	62
J	Nil	,,	300	1.02	102

The results presented in Table IV clearly indicate that at the distillate volume of 100 to 200 c.c., the recovery of nicotine is only limited to 60-70%. Full recovery was made with the minimum volume of 300 c.c. of the distillate, an observation in contradiction to Ganz (*Bot. Gaz.*, 1951, **113**, 195) who mentioned that nicotine was fully recovered even when the distillate was collected to 150-200 c.c.

This investigation was supported by the grant of the Indian Council of Medical Research to whom authors' thanks are due.

Departments of Pharmacology and Biochemistry,
M. G. M. Medical College,
Indore (M. B.).

Received April 22, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

PECHMANN REACTION: COUMARINS FROM 2-ETHYLQUINOL AND 4-ETHYLPYROGALLOL

By D.H. Mehta, R.S. Salimath and N.M. Shah

2-Ethylquinol and 4-ethylpyrogallol have been condensed with various β-ketonic esters and the respective coumarins obtained are described. The results show that these phenols are more reactive than quinol and pyrogallol respectively.

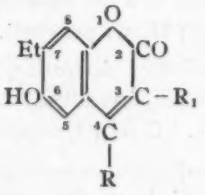
The Pechmann condensation of resorcinol and its various derivatives with different β-ketonic esters has been extensively investigated (Sethna and Shah, *Chem. Rev.*, 1945, **36**, 1). Hardly any work on similar lines is available on quinol and pyrogallol derivatives.

Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1942, **15A**, 11) unsuccessfully attempted the condensation of quinacetophenone with acetoacetic ester (vide Shah and Shah, *J. Chem. Soc.*, 1938, 1425) and further found that 2-bromoquinol was unreactive; 2 chloroquinol was less reactive but 2-methyl- and 2-ethylquinols were more reactive. In the case of pyrogallol derivatives, the same authors (*loc. cit.*, p.1) found that generally they were less reactive than those of resorcinol.

The work described in this paper was undertaken with a view to ascertaining the effect of 2-ethyl group in quinol nucleus and 4-ethyl group in pyrogallol nucleus respectively on the Pechmann reaction with β-ketonic esters other than those described by Desai and Mavani (*loc.cit.*). On repeating the condensation of 2-ethylquinol with the β-ketonic esters used by the previous workers, we obtained the same coumarins; but phosphorus oxychloride was found to be a better condensing agent than sulphuric acid, used by the previous workers.

We have now condensed 2-ethylquinol (I) with (*i*) acetone dicarboxylic acid, (*ii*) ethyl acetosuccinate and (*iii*) ethyl-α-*n*-butyl acetoacetate in presence of sulphuric acid as well as of phosphorus oxychloride, the corresponding coumarins (II) being obtained in good yields with the latter agent.

(I)

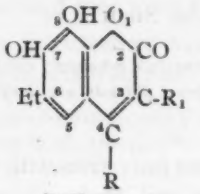


(II)

[(*i*). $R_1 = H$; $R = -CH_2.COOH$. (*ii*). $R_1 = -CH_2.COOEt$ or $-CH_2COOH$; $R = Me$. (*iii*). $R_1 = n$-butyl; $R = Me$]

It is thus evident that the reactivity of hydroquinone molecule is enhanced by 2-ethyl group, as borne out by the readiness with which it forms coumarins with various substituted β-ketonic esters, in comparison with less reactive quinol.

Similarly, 4-ethylpyrogallol was condensed with the above two β-ketonic esters as well as ethyl α-(α-hydroxy-βββ-trichloroethyl)-acetoacetate. It was also condensed with malic acid in presence of sulphuric acid. All the new coumarins (III) and their derivatives are described in the Experimental.



(III)

(*i*). R_1 = H ; R = -CH_2.COOH.
(*ii*). R_1 = -CH_2.COOEt or -CH_2.COOH ; R = Me.
(*iii*). R_1 = -CH(OH)C.Cl_3 ; R = Me.
(*iv*). R_1 = R = H.

The results show that phosphorus oxychloride is more efficient than sulphuric acid as a condensing agent. It effects the condensation with better yields where sulphuric acid fails. Desai and Mavani (*loc. cit.*) observed that the derivatives of pyrogallol were less reactive than those of resorcinol. 4-Ethyl substituent, though not inhibitory, reduces reactivity of the pyrogallol nucleus as the coumarins are obtained in low yields.

EXPERIMENTAL

Coumarins derived from 2-Ethylquinol

2-Ethylquinol required for this investigation was prepared by the Clemmensen reduction of quinacetophenone.

6-Hydroxy-7-ethyl-4-methylcoumarin.—To 2-ethylquinol (5 g.) and acetoacetic ester (5 g.) $POCl_3$ (3 c.c.) was added with cooling under tap. After keeping it at room temperature overnight it was treated with ice ; the solid obtained was collected and crystallised from alcohol in needles, m.p. 200°, yield 4.5 g., identical with Desai and Mavani's product (*loc. cit.*).

The *benzoyl derivative*, prepared by benzoyl chloride-pyridine method, crystallised from alcohol in white needles, m.p. 150°. (Found : C, 73.1 ; H, 5.3. $C_{19}H_{16}O_4$ requires C, 73.2 ; H, 5.2 per cent).

The *methoxy derivative*, prepared by acetone-dimethyl sulphate-sodium bicarbonate method, crystallised from alcohol in white needles, m.p. 165°. (Found : C, 71.4 ; H, 5.5. $C_{13}H_{14}O_3$ requires C, 71.5 ; H, 6.4 per cent).

6-Hydroxy-7-ethylcoumarin-4-acetic Acid.—To a cooled solution of acetone dicarboxylic acid from citric acid (12.5 g.) and H_2SO_4 (conc., 25 c.c.) 2-ethylquinol (7 g.) was added in small lots, and the mixture was left overnight in an ice-box. On decomposing with ice, the solid obtained was collected and treated with sodium bicarbonate and filtered. The filtrate on acidification furnished the acid, which crystallised from acetic acid in white needles, m.p. 192° (decomp.), yield 7 g. (Found : C, 62.8 ; H, 4.7 ; equiv., 246.3. $C_{13}H_{12}O_5$ requires C, 62.9 ; H, 4.8 per cent. Equiv., 246).

The *acetyl derivative*, prepared as usual, crystallised from alcohol in needles, m.p. 182° (decomp.). (Found: C, 61.9; H, 4.8. $C_{15}H_{14}O_5$ requires C, 62.1; H, 4.8 per cent).

The *methyl ester* crystallised from alcohol in needles, m.p. 185°. (Found: C, 63.9; H, 5.1. $C_{14}H_{14}O_5$ requires C, 64.1; H, 5.3 per cent).

The *ethyl ester*, prepared as usual, melted at 188°. (Found: C, 65.1; H, 5.8. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.8 per cent).

Decarboxylation.—The acid was heated at 195° for 15 minutes. After effervescence had subsided, the residue was cooled and crystallised from alcohol in needles, m.p. 200°; mixed m.p. with 6-hydroxy-7-ethyl-4-methylcoumarin was undepressed.

6-Hydroxy-7-ethyl-4-methylcoumarin-3 acetic Acid and its Ethyl Ester

(*i*). To 2-ethylquinol (3 g.) and ethyl acetosuccinate (5 g.) H_2SO_4 (conc., 12 c.c.) was added with cooling; the mixture was left overnight at room temperature and then treated with ice. The solid was filtered off and treated with sodium bicarbonate solution. A part of it dissolved; it was filtered. The residue was crystallised from alcohol in light brownish needles, m.p. 189°, yield 2 g. (Found: C, 66.1; H, 6.1. $C_{16}H_{18}O_5$ requires C, 66.2; H, 6.2 per cent).

The filtrate was acidified and the solid was crystallised from glacial acetic acid in shining plates, m.p. 285°, yield 0.7 g. (Found: C, 63.9; H, 5.1; equiv., 261. $C_{14}H_{14}O_5$ requires C, 64.1; H, 5.3 per cent. Equiv., 262).

The above condensation was repeated using 80% H_2SO_4 with the same results as above.

(*ii*). The above condensation was repeated using $POCl_3$, when a large quantity of the ester, m.p. 189°, was obtained.

Hydrolysis.—The ester was hydrolysed by alcoholic sodium hydroxide (10%) when the acid, m.p. 285°, was obtained, identical with the acid described above.

Derivatives of the Ester.—The *acetyl derivative*, crystallised from alcohol in needles, m.p. 126°. (Found: C, 65.0; H, 5.9. $C_{18}H_{20}O_6$ requires C, 65.1; H, 6.0 per cent).

The *benzoyl derivative* crystallised from alcohol in long needles, m.p. 145°. (Found: C, 70.1; H, 5.6. $C_{23}H_{22}O_6$ requires C, 70.0; H, 5.6 per cent).

The *methoxy derivative*, prepared as usual, crystallised from alcohol in needles, m.p. 169°. (Found: C, 66.7; H, 6.5. $C_{17}H_{20}O_5$ requires C, 67.1; H, 6.6 per cent).

Derivatives of the Acid.—The *ethyl ester* was found identical with the above condensation product. The *acetyl derivative* crystallised from alcohol in white needles, m.p. 215°. (Found: C, 62.9; H, 5.2. $C_{16}H_{16}O_6$ requires C, 63.2; H, 5.3 per cent).

The *decarboxylation* was carried out as before. The product, m.p. 245°, was found identical with 6-hydroxy-7-ethyl-3:4-dimethylcoumarin.

6-Hydroxy-7-ethyl-3:4-dimethylcoumarin.—2-Ethylquinol (3 g.) and ethyl-α-methyl acetoacetate (4 g.) were treated with $POCl_3$ (3 c.c.) with cooling under tap. The reaction mixture was left overnight at room temperature and then poured over ice. A solid separating was crystallised from alcohol in white plates, m.p. 245°, yield 3 g. Desai and Mavani (*loc. cit.*) report m.p. 239°. (Found: C, 71.3; H, 6.3. Calc. for $C_{13}H_{14}O_3$: C, 71.6; H, 6.4 per cent).

The *acetyl derivative* crystallised from alcohol in white needles, m.p. 149°. Desai and Mavani (*loc. cit.*) report m.p. 150°.

The *benzoyl derivative* was obtained in white needles from alcohol, m.p. 137°. (Found : C, 74.5 ; H, 5.5. $C_{20}H_{16}O_4$ requires C, 74.5 ; H, 5.6 per cent).

The *methoxy derivative* crystallised from dilute alcohol, m.p. 188°. (Found : C, 72.8 ; H, 6.9. $C_{14}H_{16}O_3$ requires C, 73.0 ; H, 7.0 per cent).

6-Hydroxy-7-phenyl-4-methylcoumarin.—2-Ethylquinol (3 g.) was condensed with ethyl benzoylacetate (5 g.) in presence of $POCl_3$. The product crystallised from benzene in light green needles, m.p. 194°, yield 1.5 g. Desai and Mavani (*loc. cit.*) report the same melting point.

The acetyl derivative was obtained in buff-coloured needles from alcohol, m.p. 125°. (Found : C, 73.2 ; H, 5.2. $C_{16}H_{20}O_3$ requires C, 73.4 ; H, 5.2 per cent).

6-Hydroxy-7-ethyl-3-butyl-4-methylcoumarin.—2-Ethylquinol (3 g.) was condensed with ethyl-α-*n*-butyl acetoacetate (4 g.) as before. On working up the reaction mixture after 2 days, the pasty product on repeated washing with cold water afforded a solid which crystallised from benzene in light green grains, m.p. 215°, yield 2 g. (Found : C, 73.8 ; H, 7.7. $C_{16}H_{20}O_3$ requires C, 73.8 ; H, 7.7 per cent).

The *acetyl derivative* crystallised from alcohol in white needles, m.p. 150°. (Found : C, 71.3 ; H, 7.0. $C_{18}H_{22}O_4$ requires C, 71.5 ; H, 7.3 per cent).

Coumarins derived from 4-Ethylpyrogallol

4-Ethylpyrogallol was prepared by the Clemmensen reduction of gallacetophenone. 4-Ethylpyrogallol on condensation with ethyl acetoacetate in presence of (*i*) $AlCl_3$ in nitrobenzene and (*ii*) $POCl_3$ yielded 7 : 8-dihydroxy-6-ethyl-4-methylcoumarin, m.p. 204°. Desai and Mavani (*loc.cit.*, p. 4) report the same melting point.

Formation of 7 : 8-Dihydroxy-6-ethylcoumarin-4-acetic Acid.—To ice-cooled acetone dicarboxylic acid from citric acid (8 g.) and H_2SO_4 (10 c.c.) 4-ethylpyrogallol (3 g.) was added with more H_2SO_4 (5 c.c.), the reaction mixture being left overnight in an ice box. On treatment with ice the product obtained was treated with sodium bicarbonate, filtered, the filtrate acidified and the resulting acid crystallised from acetic acid in long soft needles, m.p. 215-16° (decomp.), yield 2 g. (Found : C, 59.4 ; H, 5.0. $C_{13}H_{12}O_6$ requires C, 59.1 ; H, 4.5 per cent).

The *diacetyl derivative*, prepared by acetic anhydride—H_2SO_4 drop method, crystallised from dilute alcohol in colorless granules, m.p. 202-203°. (Found : C, 58.2 ; H, 4.8. $C_{17}H_{16}O_8$ requires C, 58.6 ; H, 4.6 per cent).

The *dibenzoyl derivative*, prepared by Schotten-Baumann method, crystallised from alcohol in small needles, m.p. 110°. (Found : C, 68.4 ; H, 3.9. $C_{27}H_{20}O_8$ requires C, 68.6 ; H, 3.9 per cent).

The *dimethoxy derivative*, prepared by acetone-K_2CO_3-dimethyl sulphate method, crystallised from water in white soft needles, m.p. 112°. (Found : C, 61.2, H, 5.7. $C_{15}H_{16}O_6$ requires C, 61.6 ; H, 5.4 per cent).

The *ethyl ester* was prepared by refluxing the coumarin-4-acetic acid (3 g.), alcohol (20 c.c.) and H_2SO_4 (1 c.c.) for 15 hours. It crystallised from alcohol in long colorless needles, m.p. 212-13°. (Found: C, 61.2; H, 5.8. $C_{15}H_{16}O_6$ requires C, 61.6; H, 5.5 per cent).

The *acetyl derivative* of the above ester, prepared as before, crystallised from alcohol in small needles, m.p. 100°. (Found: C, 60.1; H, 5.5. $C_{19}H_{20}O_8$ requires C, 60.6; H, 5.3 per cent).

The *methoxy derivative* of the above ester, prepared by acetone-sodium bicarbonate-dimethyl sulphate method, crystallised from alcohol in colorless needles, m.p. 158°. (Found: C, 63.5; H, 6.1. $C_{17}H_{20}O_6$ requires C, 63.7; H, 6.2 per cent).

4-Ethylpyrogallol was condensed with ethyl acetosuccinate in presence of (*i*) H_2SO_4 (80%) and (*ii*) $POCl_3$. The yield is poor in (*i*) and nearly quantitative in (*ii*). Ethyl 7:8-dihydroxy-6-ethyl-4-methylcoumarin-3-acetate crystallised from benzene in colorless needles, m.p. 152°. Shah and Shah (this *Journal*, 1942, **19**, 489) have reported the same melting point.

Hydrolysis.—The ester was hydrolysed by HCl (conc.). 7:8-Dihydroxy-6-ethyl-4-methylcoumarin-3-acetic acid crystallised from acetic acid, m.p. 275°, identical with that of Shah and Shah (*loc. cit.*).

4-Ethylpyrogallol on condensation with ethyl benzoylacetate in presence of H_2SO_4 (80%) furnished 7:8-dihydroxy-6-ethyl-4-phenylcoumarin, m.p. 145° (Desai and Mavani, *loc. cit.*, p. 4).

4-Ethylpyrogallol on condensation with α-(α-hydroxy-βββ-trichloro-ethyl)-acetoacetate in presence of $POCl_3$ afforded 7:8-dihydroxy-6-ethyl-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarin, identical with that of Shah and Kulkarni (*J. Univ. Bom.*, 1941, **10**, Pt. III, 120).

The *tribenzoyl derivative*, prepared by Schotten-Baumann method, crystallised from dilute alcohol in colorless granules, m.p. 103°. (Found: C, 61.6; H, 3.5. $C_{33}H_{23}O_8Cl_3$ requires C, 61.8; H, 3.7 per cent).

The *trimethoxy derivative*, prepared as before, crystallised from alcohol in small needles, m.p. 144-45°. (Found: C, 49.6; H, 4.5. $C_{17}H_{19}O_5Cl_3$ requires C, 49.8; H, 4.6 per cent).

Condensation of 4- Ethylpyrogallol with Malic Acid

4-Ethylpyrogallol (3 g.), malic (3 g.) and H_2SO_4 (20 c.c.) were mixed and heated on a water-bath for 1 hour. On treating the mixture with water, the mass became pasty which was repeatedly washed with cold water. On crystallisation first from dilute alcohol and then from water, pale yellow needles were obtained, m.p. 171-72°, yield 1 g. (Found: C, 63.8; H, 4.6. $C_{11}H_{10}O_4$ requires C, 64.1; H, 4.8 per cent).

The *diacetyl derivative*, prepared by acetic anhydride—NaAc method, crystallised from dilute alcohol in pale yellow needles, m.p. 140°. (Found: C, 64.1; H, 4.9. $C_{15}H_{14}O_6$ requires C, 64.3; H, 5.0 per cent).

M. R. Science Institute,
Gujarat College,
Ahmedabad-6.

Received August 1, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

SYNTHESIS OF 6-HALOGENATED 2 : 3-DISUBSTITUTED QUINAZOL-4-ONES. PART III*

By R. S. Salimath, S. R. Patel and N. M. Shah

Synthesis of-6-chloro- and 6-bromo-2-methyl-3-substituted phenylquinazol-4-ones is described.

The present investigation is an extension of our previous work on synthesis of differently benz-substituted quinazolone derivatives (this *Journal*, 1955, **32**, 199, 483). A contributory factor to the medicinal properties of some well-known drugs like atebrine, paludrine, chloromycetin is attributed to the presence of chlorine as a substituent in their respective molecules. Further, the products obtained by the chemical investigation of *Arboria correa*, a plant known for its medicinal efficacy in Ayurveda have been found to be 2 : 3-substituted quinazolone derivatives (Mrs. D. Chakravarti and co-workers, *J. Chem. Soc.*, 1953, 3337). Hence, it was considered worthwhile to synthesise such quinazolone derivatives with chlorine as a substituent in the benzene ring of the quinazolone molecule. Analogous quinazolone derivatives with bromine as a substituent have also been synthesised.

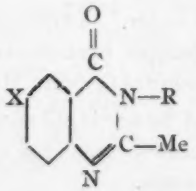
Arrangements are being made to screen these compounds for their medicinal properties.

These 6-chloro- or 6-bromo-2 : 3-substituted quinazolones have been obtained by condensing N-aceto-5-chloro- or -5-bromo-anthranilic acid with different amines, following the method already described in our previous communication (*loc. cit.*). 5-Chloro-N-acetoanthranilic acid required for the purpose was obtained by chlorination of N-aceto-*o*-toluidide followed by oxidation of 2-acetamino-5-chlorotoluene, using neutral potassium permanganate (Tomisek and Christiansen, *J. Amer. Chem. Soc.*, 1948, **70**, 2424). 5-Bromo-N-acetoanthranilic acid was similarly prepared (Bogert and Hand, *ibid.*, 1905, **27**, 1480).

All the quinazolones described in this paper have been reported for the first time excepting 3-phenyl- and 3-*o*-tolyl-6-bromo-2-methylquinazol-4-ones (Bogert and Hand, *ibid.*, 1906, **28**, 103).

Experimental

6-Chloro- and 6-bromo-quinazol-4-ones obtained are described in a tabular form to avoid repetition.



[X = Cl or Br ; R = substituted phenyl group].

* The first two papers on this subject are to be considered as Part I and Part II of this series.

TABLE I

TABLE I

6-Chloro-2-methyl-3-(R)-substituted quinazol-4-ones and their hydrochlorides.

	R =	M.P.	Crystalline form.	Formula.	Analysis: Found.	Calc.
1.	$-C_6H_5$	163°	Pale yellow small needles	$C_{15}H_{11}ON_2Cl$	N, 9.8% Cl, 12.7	N, 10.4% Cl, 13.1
	Hydrochloride of 1	241°	Colorless small needles	$C_{15}H_{11}ON_2Cl.HCl$	Equiv. 304.0	Equiv. 307.0
2.	$-C_6H_4.OCH_3$ (*p*)	172°	Straw coloured granules	$C_{16}H_{13}O_2N_2Cl$	N, 8.9% Cl, 11.6	N, 9.3% Cl, 11.8
	Hydrochloride of 2	237° (decomp.)	Light white granules	$C_{16}H_{13}O_2N_2Cl.HCl$	Equiv. 335.5	Equiv. 337.0
3	$-C_6H_4.CH_3$ (*o*)	167°	Light white granules	$C_{16}H_{13}ON_2Cl$	N, 9.4% Cl, 12.3	N, 9.8% Cl, 12.5
	Hydrochloride of 3	238° (decomp.)	Small plates	$C_{16}H_{13}ON_2Cl.HCl$	Equiv. 317.3	Equiv. 321.0
4.	$-C_6H_4.CH_3$ (*m*)	179°	Pale yellow soft needles	$C_{16}H_{13}ON_2Cl$	N, 9.3% Cl, 12.3	N, 9.8% Cl, 12.5
5.	$-C_6H_4.CH_3$ (*p*)	104°	White shining plates	$C_{16}H_{13}ON_2Cl$	N, 9.2 Cl, 12.2	N, 9.8 Cl, 12.5
	Hydrochloride of 5	235° (decomp.)	White granules	$C_{16}H_{13}ON_2Cl.HCl$	Eqniv. 318.1	Equiv. 321.0
6.	$-C_6H_4.Cl$ (*o*)	158°	White lustrous granules	$C_{15}H_{10}ON_2Cl_2$	N, 8.6% Cl, 22.7	N, 9.2% N, 23.3
	Hydrochloride of 6	236° (decomp.)	Colorless shining granules	$C_{15}H_{10}ON_2Cl_2.HCl$	Equiv. 336.2	Equiv. 341.5
7.	$-C_6H_4.Cl$ (*m*)	175°	Dull white needles	$C_{15}H_{10}ON_2Cl_2$	N, 8.7% Cl, 22.8	N, 9.2% Cl, 23.3
	Hydrochloride of 7	254° (decomp.)	Light white granules	$C_{15}H_{10}ON_2Cl_2.HCl$	Equiv. 336.92	Equiv. 341.5
8.	$-C_6H_4.NO_2$ (*p*)	246°	Yellowish brown needles	$C_{15}H_{10}O_3N_3Cl$	N, 13.1% Cl, 10.8	N, 13.3% Cl, 11.3
9.	$-C_6H_4.N(C_2H_5)_2$ (*p*)	210°	Bluish green needles	$C_{19}H_{20}ON_3Cl$	N, 11.8 Cl, 10.2	N, 12.3 Cl, 10.4
	Hydrochloride of 9	234° (decomp).	Small colorless needles	$C_{19}H_{20}ON_3Cl.HCl$	Equiv. 373.1	Equiv. 378.0

* Equiv. found by titrations.

TABLE II

6-Bromo-2-methyl-R-(substituted)-quinazol-4-ones and their hydrochlorides.

	R =	M.P.	Crystalline form.	Formula.	Analysis. Found.	Calc.
1.	$-C_6H_5$	186°	Pale yellowish small needles	$C_{15}H_{11}ON_2Br$	Br, 25 3%	Br, 25.4%
	Hydrochloride of 1	246° (decomp.)	small needles	$C_{15}H_{12}ON_2ClBr$	Equiv. 347.7	Equiv. 351 5
2.	$-C_6H_4.OCH_3$ (*p*)	181°	Colorless small needles	$C_{16}H_{13}O_2N_2Br$	N, 7 7% Br, 23 0	N, 8 1% Br, 23.2
	Hydrochloride of 2	233° (decomp.)	Colorless granules	$C_{16}H_{14}O_2N_2ClBr$	Equiv. 376.4	Equiv. 381.5
3.	$-C_6H_4.CH_3$ (*o*)	148°	White small needles	$C_{16}H_{13}ON_2Br$	Br, 24.1%	Br, 24.3%
	Hydrochloride of 3	241° (decomp.)	Colourless crystals	$C_{16}H_{14}ON_2ClBr$	Equiv. 361.5	Equiv. 365.5
4.	$-C_6H_4\ CH_3$ (*m*)	165°	Pale yellowish soft needles	$C_{16}H_{13}ON_2Br$	N, 8.0% Br. 24.2	N, 8.5% Br, 24.3
	Hydrochloride of 4	236° (decomp.)	Feathery plates	$C_{16}H_{14}ON_2ClBr$	Equiv. 363.2	Equiv. 365.5
5.	$-C_6H_4.CH_3$ (*p*)	131°	Yellow needles	$C_{16}H_{13}ON_2Br$	N, 8.1% Br, 23 7	N, 8.5% Br. 24 3
	Hydrochloride of 5	245° (decomp.)	Long soft needles	$C_{16}H_{14}ON_2ClBr$	Equiv. 360.4	Equiv. 365.5
6	$-C_6H_4.NO_2$ (*p*)	255°	Yellowish brown shining needles	$C_{15}H_{10}O_3N_3Br$	N, 11.5% Br, 21.7	N, 11.7% Br, 22.2
7.	$-C_6H_4.Cl$ (*o*)	176°	Lustrous granules	$C_{15}H_{10}ON_2ClBr$	N, 7 5% Total halogen, 33.0	N, 8.0% Total halogen, 33.1
	Hydrochloride of 7	237° (decomp.)	White granules	$C_{15}H_{11}ON_2Cl_2Br$	Equiv. 382.2	Equiv. 386
8.	$-C_6H_4.Cl$ (*m*)	196°	Yellowish needles	$C_{15}H_{10}ON_2ClBr$	N. 7.6% Total halogen, 32.7	N, 8.0% Total halogen, 33.1
	Hydrochloride of 8	255° (decomp.)	Long colorless needles	$C_{15}H_{11}ON_2Cl_2Br$	Equiv. 388.2	Equiv. 386
9.	$-C_6H_4.N(C_2H_5)_2$ (*p*)	227°	Yellowish green needles	$C_{19}H_{20}ON_3Br$	N, 10 3% Br, 20 2	N, 10.9% Br, 20.7
	Hydrochloride of 9	247° (decomp.)	Colorless granules	$C_{19}H_{21}ON_3ClBr$	Equiv. 417.2	Equiv. 422.5

* Equiv. found by titrations.

M. R. SCIENCE INSTITUTE, GUJARAT COLLEGE, AHMEDABAD-6.

Received August 23, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

Received August 23, 1955.

BROMINATION OF COMPOUNDS CONTAINING TWO AROMATIC NUCLEI. PART XVI. BROMINATION OF SOME ARYLAMIDES OF 2-HYDROXY-3-METHYLBENZOIC ACID (*o*-CRESOTIC ACID)

By Mrs. V. R. Patakoot and G. V. Jadhav

Bromination of anilide, *o*-, *m*- and *p*-toluidides, *o*-, *m*- and *p*-nitroanilides, *o*- and *p*-anisidides, *p*-phenetidide and *β*-naphthylamide of *o*-cresotic acid has been carried out in presence of acetic acid as well as with liquid bromine. The constitution of the bromo derivatives has been proved by hydrolysing them and identifying the acidic and basic components

Present work is the continuation of that of Jadhav and Nerlekar (*J. Univ. Bom.*, 1951, **20**, Pt. III, 97) taken up with a view to ascertaining the effect of substituting the negative $-NO_2$ group by $-CH_3$ group towards bromination. In the present work it is observed that the molecule is rendered more reactive, as by brominating the compounds as before in hot solution only, bromine is found to enter both the nuclei simultaneously, and hence, no pure bromo derivative can be isolated when the reactants are used in the proportion 1 : 1, excepting in the case of *p*-toluidide, and *o*-, *m*- and *p*-nitroanilides. With more bromine solution dibromo derivatives were obtained in all cases excepting in the case of nitroanilides. Liquid bromine furnished higher bromo derivatives excepting in the case of *o*- and *p*-toluidides

The constitutions of all the bromo derivatives have been arrived at by hydrolysing them and identifying the acidic and basic components.

Experimental

Bromination in Acetic Acid Medium.—The arylamide (1 g.) was dissolved in boiling acetic acid and 50% solution of bromine in acetic acid was added to it excepting in the case of *β*-naphthylamide where the addition was done at 70° to 80°. Bromo product began to separate as the reaction mixture cooled down. The products are described in Table I. The yield of the bromo derivatives varied from 1.5 to 1.8 g.

Bromination with Liquid Bromine.—The arylamide (2 g.) was gradually added to liquid bromine (3 c.c.) and the reaction mixture was left overnight at room temperature, when the solid went into solution. The solution was then diluted with water and the solid obtained was triturated with sodium bisulphite solution to remove excess of bromine. It was then crystallised from a suitable solvent. The compounds are described in Table II.

Hydrolysis.—The bromo derivatives excepting those of *o*- and *p*-anisidides, *p*-phenetidide and *β*-naphthylamide were hydrolysed by boiling with 10% solution of NaOH (100 c.c. for 1 g.) for several hours, as mentioned against the respective compound in the table. The mixture was then diluted and extracted with ether. The base obtained from ether was identified by mixed melting point with genuine specimens excepting in the case of bromo-*p*-toluidine and bromo-*p*-anisidine which were identified through their acetyl derivatives.

TABLE I

[B represents 2-hydroxy-3-methyl-benz-. B-5-B represents 2-hydroxy-3-methyl-5-bromo- benz-].

Amide used.	Acetic acid.	Bromine soln.	Bromo derivative.	Cryst. shape.	M.P.	Formula.	% Bromine Found.	% Bromine Calc.	Period of heating for hydrolysis.
B-anilide	30 c.c.	6.0 c.c.	B-5-B-4′-bromo-anilide *	White needles	162-63°	$C_{14}H_{11}O_2NBr_2$	41.7	41.6	8 hr.
B-*o*-toluidide	15	5.2	B-5-B-4′-bromo-*o*-toluidide †	,, plates	154-55°	$C_{15}H_{13}O_2NBr_2$	40.4	40.1	7
B-*m*-toluidide	40	5.2	B-5-B-4′-bromo-*m*-toluidide *	,, needles	162-63°	$C_{15}H_{13}O_2NBr_2$	40.2	40.1	6
B-*p*-toluidide	30	2.5	B-5-B-*p*-toluidide *	,, ,,	162-63°	$C_{15}H_{14}O_2NBr$	25.2	25.0	12
B-*p*-toluidide	30	5.2	B-5-B-2′-bromo-*p*-toluidide ‡	Pinkish needles	204-5°	$C_{15}H_{13}O_2NBr_2$	40.2	40.1	14
B-*o*-nitroanilide	40	3	B-5-B-*o*-nitroanilide *	Yellow needles	184-85°	$C_{14}H_{11}O_4N_2Br$	23.1	22.8	8
B-*m*-nitroanilide	40	3	B-5-B-*m*-nitroanilide *	White plates	210-11°	$C_{14}H_{11}O_4N_2Br$	22 6	22.8	6
B-*p*-nitroanilide	60	3	B-5-B-*p*-nitroanilide *	Greenish plates	265-66°	$C_{14}H_{11}O_4N_2Br$	22.7	22.8	8
B-*o*-anisidide	30	5	B-5-B-5′-bromo-*o*-anisidide†	White needles	145-46°	$C_{15}H_{13}O_3NBr_2$	38.5	38 6	7
B-*p*-anisidide	30	9	B-5-B-3′-bromo-*p*-anisidide†	Do	185-86°	$C_{15}H_{13}O_3NBr_2$	38.4	38.6	6
B-*p*-phenetidide	20	5	B-5-B-3′-bromo-*p*-phenetidide ‡	Do	184-85°	$C_{16}H_{15}O_3NBr_2$	37.2	37 3	7
B-*β*-naphthylamide	25	5	B-5-B-1′-*β*-naphthylamide ‡	Yellow needles	145-46°	$C_{18}H_{13}O_2NBr_2$	36.6	36.8	6

* Crystallised from alcohol.
† ,, ,, dil. alcohol.
‡ ,, ,, acetic acid.

TABLE II

[B represents 2-hydroxy-3-methyl-benz- and B-5-B represents 2-hydroxy-3-methyl-5-bromo-benz-].

Amide used.	Bromo derivative.	Cryst. shape.	M. P.	Formula.	% Bromine. Found.	% Bromine. Calc.	Period of heating for hydrolysis.
B-anilide	B-5-B-2′ :4′-dibromoanilide	White plates	197-98°	$C_{14}H_{10}O_2NBr_3$	51.5	51.7	12 hr.
B-*m*-toluidide	B-5-B-4′ :6′-dibromotoluidide	,, needles	183-84°	$C_{15}H_{13}O_2NBr_2$	50.2	50.2	16
B-*p*-toluidide	B-5-B-2′-bromo-*p*-toluidide	Pinkish needles	204°	$C_{15}H_{13}O_2NBr_2$	40.2	40.0	14
B-*o*-nitroanilide	B-5-B-3′-bromo-2′-nitroanilide	Yellow needles	168-69°	$C_{14}H_{10}O_4N_2Br_2$	37.4	37.2	10
B-*m*-nitroanilide	B-5-B-6′-bromo-3′-nitroanilide	White needles	205-6°	$C_{14}H_{10}O_4N_2Br_2$	37.3	37.2	8
B-*p*-nitroanilide	B-5-B-2′-bromo-4′-nitroanilide	Brown needles	240-41°	$C_{14}H_{10}O_4N_2Br_2$	37.1	37.2	10
B-*o*-anisidide	B-5-B-5′ :6′-dibromo-*o*-anisidide	Light red needles	149-50°	$C_{15}H_{12}O_3NBr_3$	48 7	48.6	8
B-*p*-anisidide	B-5-B-2′ :5′-dibromo-*p*-anisidide	White needles	215-16°	$C_{15}H_{12}O_3NBr_3$	48.5	48.6	7
B-*p*-phenetidide	B-5-B-2′ :5′-dibromo-*p*-phenetidide	Do	245-46°	$C_{16}H_{14}O_3NBr_3$	47 4	47.2	7
B-*β*-naphthylamide	B-5-B-1′ :3′-6′-tribromo-*β*-naphthylamide	Yellow needles	163-64°	$C_{18}H_{11}O_2NBr_4$	53-7	53 9	8

All bromo derivatives in Table II were crystallised from acetic acid except that of *o*-nitroanilide which was crystallised from alcohol and that of *o*-anisidide which was crystallised from dilute acetic acid. Yields of bromo derivatives were between 1.7 to 2 g.

The acid obtained from the alkaline solution on acidification was always found to be 2-hydroxy-3-methyl-5-bromobenzoic acid.

In the case of the bromo derivatives of *o*- and *p*-anisidides, *p*-phenetidide and *β*-naphthylamide, hydrolysis was carried out by heating on a boiling water-bath with 80 % H_2SO_4 (30 to 50 c.c. was used for 2 g.) for several hours. The reaction mixture was then diluted and the solid obtained was filtered. The filtrate on neutralisation afforded the base which was extracted with ether. The solid obtained from ether was identified by mixed melting point with genuine specimens.

The solid, insoluble in acidic solution, was then extracted with sodium bicarbonate solution and the acid was precipitated from it on acidification. It was identified as 2-hydroxy-3-methyl-5-bromobenzoic acid.

ORGANIC CHEMISTRY LABORATORY,
INSTITUTE OF SCIENCE, BOMBAY.

Received August 22, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

ON THE QUANTITATIVE ESTIMATION OF BERYLLIUM. PART I. AS BARIUM FLUOBERYLLATE GRAVIMETRICALLY

By R. K. Duttta and A. K. Sen Gupta

A gravimetric method for the estimation of beryllium has been described. Beryllium with fluoride ion affords a BeF_4^{2-} ion, and when a barium salt is added to this solution, it effects a quantitative precipitation of $BaBeF_4$. The p_H of the solution was maintained at approx. 4. The formation of barium fluoride and the corroding action of hydrofluoric acid on glass are prevented by addition of boric acid.

There are several gravimetric, volumetric and colorimetric methods for the estimation of beryllium. In the gravimetric methods beryllium is either weighed as BeO or $Be_2P_2O_7$. In the methods where beryllium is weighed as BeO by ignition, it is precipitated as $Be(OH)_2$ by ammonia gas or by ammonium nitrite and methyl alcohol (Moser and Singer, *Monatsh.*, 1927, **48**, 675) or by other hydrolytic reagents (Akiyama, *Japan Analyst*, 1953, **2**, 116 ; Quadrat and Svejda, *Chem. Obzor.*, 1950, **25**, 85) or as tannin complex (Moser and Niessner, *Monatsh.*, 1927, **48**, 113). Beryllium is also weighed as $Be_2P_2O_7$ by ignition, after precipitating as $BeNH_4PO_4$ (Moser and Singer, *ibid.*, 1927, **48**, 679).

From the analogy between SO_4^{2-} ion and BeF_4^{2-} ion (Sarkar and Ray, this *Journal*, 1929, **6**, 987), it was presumed that a method might be developed for the estimation of beryllium on account of sparing solubility of $BaBeF_4$ like $BaSO_4$. In the present communication, a new method for the gravimetric estimation of beryllium has been described, in which beryllium is weighed as $BaBeF_4$.

Principle of the Method.—Beryllium ion with fluoride ion forms a very stable BeF_4^{2-} ion, according to the equation

$$Be^{2+} + 4F^- = BeF_4^{2-}.$$

The fluoberyllate ion is then precipitated as $BaBeF_4$ by adding barium salt.

$$BeF_4^{2-} + Ba^{2+} = BaBeF_4.$$

It is known that barium affords sparingly soluble BaF_2 from alkali fluoride solutions. But in the presence of boric acid no precipitate of BaF_2 was found to occur below $p_H \approx 5$. So, it is necessary to make the precipitation of $BaBeF_4$ at p_H lower than 5. Again, if p_H of fluoride solution is lowered, the action of hydrofluoric acid on glass containers also increases, leading to the formation of silico-fluoride ion which provides sparingly soluble precipitate with barium ion.

In the present method the solution was maintained at $p_H \approx 4$. The action of hydrofluoric acid on glass container was prevented by the addition of boric acid, which also inhibited the formation of BaF_2 at this p_H. It was found, however, that $BaBeF_4$ could be precipitated quantitatively at a p_H as low as 2.5 when the concentration of fluoride in solution was low.

EXPERIMENTAL

Beryllium nitrate solution was prepared by dissolving Schering and Kahlbaum's beryllium nitrate and standardised in the usual way by precipitating beryllium as $Be(OH)_2$ by ammonia gas and estimating as BeO.

Sodium fluoride (2.5% ; Pure, E. Merk) was heated at 900°-1000° for several hours to break silico-fluoride. It was then powdered and a solution was made. It was filtered through a fine filter paper and was stored in polyethylene bottle. All the other reagents used were of G.R. quality.

Procedure.—Beryllium nitrate solution (10 c. c.) containing 22 mg. to 7 mg of beryllium was taken in a 400 c. c. beaker ; 5 drops of Wesselow's indicator and then 50 c. c. of 2.5% sodium fluoride solution were added. The volume of the solution was made to 300 c. c. and to it 4 g. of boric acid was added and stirred to dissolve it. Hydrochloric acid solution was then added to the above solution until its green colour had changed to violet. The solution was heated to boiling and 15 c.c. of hot barium chloride solution added dropwise with stirring. The solution was then kept on a hot water-bath for one hour, covering the beaker with a clock-glass which helped in maintaining the volume of the solution almost constant. The solution was stirred several times during this period. The precipitate settled down in one hour and the solution was filtered through a sintered glass crucible by suction. The precipitate was taken into the crucible by hot water and was washed till the issuing filtrate was free of chloride. Generally, washing for 8 to 10 times with 4 c. c. of water at a time was sufficient. Then it was washed twice with alcohol. The $BaBeF_4$ was dried at 110°-120° for one hour and cooled and weighed to a constant weight. It was found that one hour's drying gave constant weight.

TABLE I

Be taken	2.5% NaF soln.	Boric acid.	$BaBeF_4$ found.	Be calc. *	%Error.
21.58 mg.	50 c.c.	0.5 g.	0.5320 g.	21.52 mg.	−0.28
,,	,,	,,	0.5353	21.66	+0.37
,,	,,	1.0	0.5311	21.49	−0.42
,,	,,	,,	0.5301	21.45	−0.60
15.15	40	0.35	0.3724	15.07	−0.53
,,	,,	,,	0.3747	15.16	+0.07
,,	,,	2.0	0.3748	15.17	+0.13
,,	,,	,,	0.3737	15.12	−0.20
,,	,,	4.0	0.3743	15.15	±0
,,	,,	,,	0.3744	15.15	±0
,,	,,	6.0	0.3729	15.09	−0.40
,,	60	0.37	0.3769	15.25	+0.66
,,	100	5.0	0.3722	15.06	−0.60
,,	,,	,,	0.3758	15.20	+0.33
7.575	,,	,,	0.1881	7.610	+0.46
,,	,,	,,	0.1862	7.534	−0.54

* From the weight of $BaBeF_4$ found.

The anions (such as sulphate, silicofluoride, etc.), which produce insoluble precipitates with barium, and the cations, which afford insoluble fluorides at a p_H lower than 5, should not be present in the solution. Potassium fluoride must not be used as the source of fluoride because it forms with boric acid KBF_4 which being sparingly soluble and isomorphous with $BaBeF_4$ precipitates with it. The amount of fluoride added should be about 1 to 2 g. in the total volume of solution. Because it was seen that at higher concentrations of fluoride than 2.5 g. in the total volume of solution, error was more than 1%. The results are shown in Table I.

Further work on the estimation of beryllium in beryl is under investigation and will be shortly published.

The authors' best thanks are due to Prof. P. B. Sarkar, Dr. es. Sc., F. N. I., Ghosh Professsor and Head of the Department of Pure Chemistry, University of Calcutta, for his encouragement and suggestions in the work. They are also indebted to Sri N. N, Ghosh of Pure Chemistry Department for his helpful criticisms and suggestions.

INORGANIC CHEMISTRY LABORATORY,
DEPARTMENT OF PURE CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA-9.

Received August 8, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

APPLICATION OF REFRCTIVE INDEX IN THE STUDY OF CHEMICAL CONSTITUTION. PART I. DETERMINATION OF TRANSITION POINT OF CERTAIN HYDRATED INORGANIC SALTS IN SOLUTION BY REFRACTIVE INDEX

By Shiam Sunder Joshi and D. P. Joshi

Refractive index determinations of aqueous solutions of hydrated inorganic salts of sodium carbonate between 20° and 50° and magnesium sulphate between 20° and 55° show abrupt change at certain temperatures. The transition points, thus determined, agree with the values determined by other methods.

Some inorganic salts, when crystallised out from aqueous solutions between certain temperature ranges, separate out with different amounts of water of crystallisation. The particular temperatures at which the degree of hydration changes have been found out by various methods; among these the solubility method has been used quite often. Other methods, such as, dilatometric, thermometric, viscometric, E.M.F. etc., have also been employed. The transition points, determined by different methods, are invariably quite close, though not always identical.

Uniform variations in the values of some physical properties of pure liquids have been noticed with rise of temperature, except at temperatures where changes in constitution take place. Salts in solution behave similarly. When solutions are heated to certain temperatures, their composition has been observed to change irregularly in values. This has been utilised for determination of their transition points. Thus, in case of sodium sulphate solutions, Gibson (*J. Phys. Chem.*, 1927, **31**, 496) from density measurements, and Glass and Madgine (*J. Chem. Soc.*, 1934, 1124) from viscosity determinations presumed the existence of different hydrates between certain temperature ranges by studying the variations in the values of these properties, although no marked change at the transition point was observed by them. Dunstan and Langton (*J. Chem. Soc.*, 1912, **101**, 418) in the cases of saturated sodium sulphate and sodium carbonate solutions and Hartshorne (*ibid.*, 1924, 2096) in the cases of sodium sulphate, disodium hydrogen phosphate and nickel sulphate, however, found out the transition temperatures from viscosity determinations. Determination of refractive index is expected to yield similar information because the former is intimately connected with the density of the solution, the theory of which has been recently worked out by Sarkar and Palit (*Indian J. Phys.*, 1953, **27**, 610).

During the present work determinations of refractive index of solutions of different concentrations of sodium chloride and sodium carbonate between 20° and 55° and of magnesium sulphate between 20° and 55° have been carried out. At certain temperatures in case of sodium carbonate and magnesium sulphate solutions, the variations were not regular; these corresponded with the transition temperatures.

In the case of sodium chloride solutions of four different concentrations ($6M$, $6M/5$, $6M/25$, $6M/125$) the variation in the refractive index with rise of temperature, as noticed

by plotting temperature against n_D^t, is throughout regular within the range 20°-50°. This shows the absence of changes in the composition of the salt in solution. In the literature also no change in the degree of hydration within this range appears to have been reported. [See graphs- I(*b*), Fig. 3 ; II(b) and III(b), Fig. 1 ; and IV(b), Fig. 4].

FIG. 1

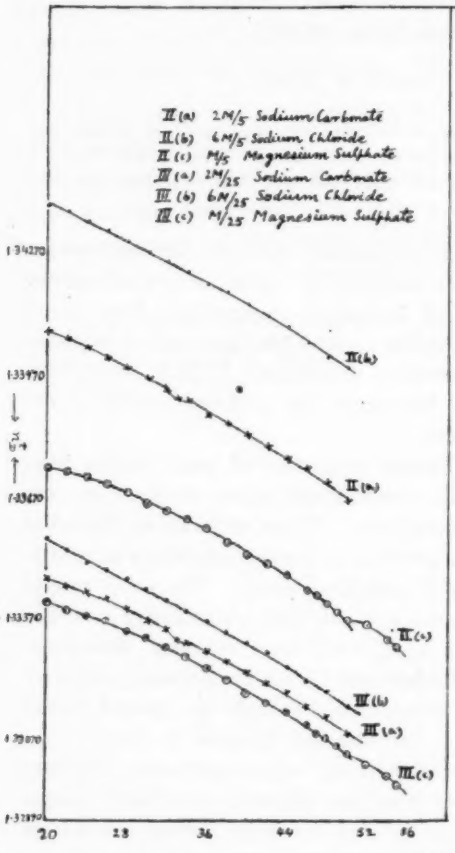
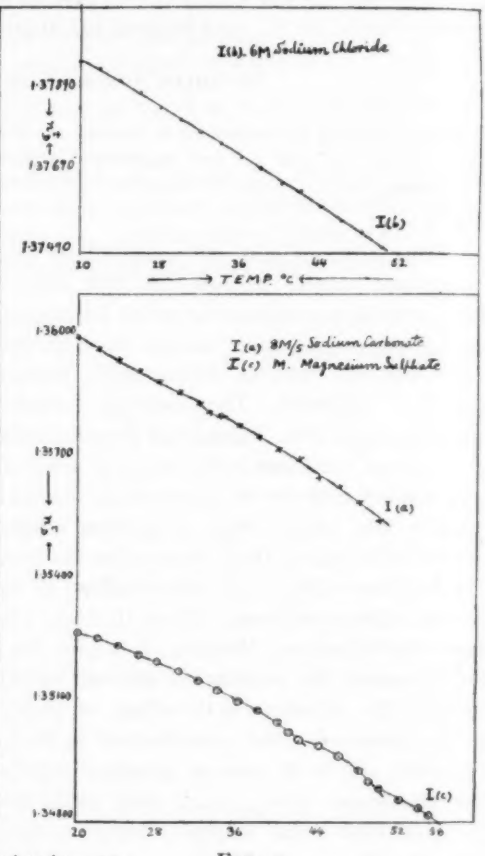


FIG. 3



Temperature →

FIG. 2

In the case of aqueous sodium carbonate solutions of four different concentrations (8*M*/5, 2*M*/5, 2M/25, 2*M*/125) it has been observed that abnormal changes in the regular variation of values take place in case of concentrated and moderately concentrated solutions (8*M*/5, 2*M*/5, 2*M*/25), once at 31.8° to 32° and again at 34.2° to 34.6°; in the case of dilute solution (2*M*/125), once at 32° and then again at 35.4°. This shows that at certain temperatures the composition of the salt changes in aqueous solution. These transition temperatures appear to be slightly influenced by concentration, as in the case of the dilute solution the second transition point is 35.4°, whereas in the more concentrated solutions it is 34.2° to 34.6° [vide graphs II(a) and III(a), Fig. 1 ; I(a), Fig. 2 and IV(a), Fig. 4].

FIG. 5

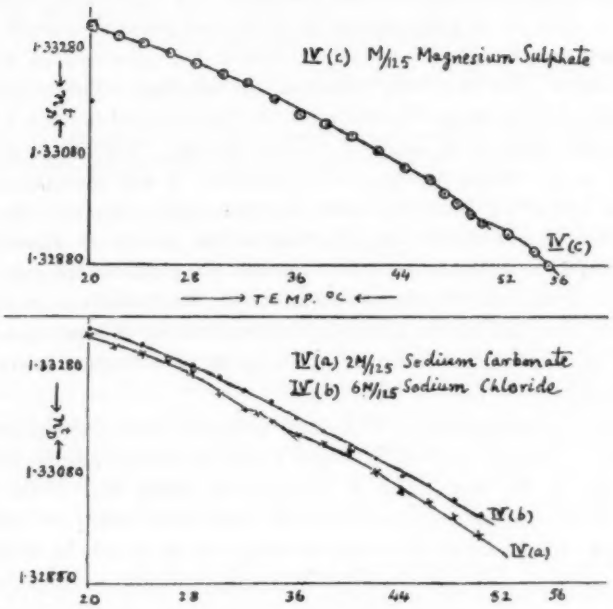


FIG. 4

Previous workers obtained by using mostly the solubility or viscometric methods similar values for transition points of different hydrates. Some of these are: (*a*) 32° the transition point between deca and heptahydrate, 35.4° between hepta and monohydrate (Richards and Fiske, *J. Amer. Chem. Soc.*, 1914, **36**, 485); (*b*) 32° between deca and stable heptahydrate, 35.37° between hepta and monohydrate and 32.96°, the metastable transition point between deca and monohydrated carbonates (Wells and McAdam, *ibid.*, 1907, **29**, 721); (*c*) 34° approximately (Tilden, *J. Chem. Soc.*, 1884, **45**, 268); (*d*) 32.5° between deca and heptahydrate, 35.4° between deca and monohydrate (Dunstan and Langton, *loc. cit.*).

In the case of the four aqueous magnesium sulphate solutions (*M*, *M*/5, *M*/25, *M*/125) also, refractive index determinations show that the transition in the composition of the salt is influenced by the temperature as also by the concentration. Two transition points, 42° and 49.4°, are observed for the nearly saturated solution (*M*), while only one, 49.4°, for the less concentrated solutions (*M*/5, *M*/25, *M*/125) [vide graphs-I(c), Fig. 2; II(c) and III(c), Fig. 1; and IV(c), Fig 5]. Some of the transition points quoted in the literature are: (*a*) 50° between heptahydrate and labile or β-hexahydrate (Wiedmann, *Wied. Ann.*, 1882, **17**, 571); (*b*) 48° to 48.5° between hepta and hexahydrate (Vander Heide, *Z. physikal. Chem.*, 1893, **12**, 418); (*c*) 48.4° between hepta and hexahydrate (Carpenter and Jette, *J. Amer. Chem. Soc.*, 1923, **45**, 578).

Experimental

Sodium chloride, anhydrous sodium carbonate and crystalline magnesium sulphate ($MgSO_4,7H_2O$) were all of A.R. quality (B.D.H.) and the same sample of conductivity water was used in all determinations. Concentrated solutions of each of them were prepared and other solutions were obtained by dilution. The refractive index was measured using a critical angle refractometer (Bellingham and Stanley Ltd.), the micro-vernier of which could read angle up to one second. Sodium lamp was used as the source of light in all measurements. The accuracy of the instrument was tested by measuring the refractive index of water, *n*-heptane and *n*-octane. The temperature of the solution under measurement was controlled within $\pm 0.2^\circ$ by allowing thermostated water of the requisite temperature to flow through the jacket of the apparatus, surrounding the solution in the cell over the mounted prism. The readings at each temperature were taken after maintaining the particular temperature for at least 15 minutes. The n_D^t, calculated out at various temperatures and graphs of refractive index of the solutions against temperature were plotted (Figs. 1-5).

Preliminary investigations with sodium sulphate and zinc sulphate have shown similar results. Further work is in progress, and attempts are being made to determine the composition of the salt while in solution at either side of the transition point. Nevertheless, there is a similarity regarding the transition point, at which the salt in solution and the solid hydrated salt undergo change in the degree of hydration.

The determination of refractive index of solution of salts of different concentrations provides an easy approach towards the study of composition changes with variation of temperature.

Chemistry Laboratories,
Meerut College,
Meerut.

Received February 4, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 2, 1956]

POSSIBLE ANTITUBERCULOUS COMPOUNDS. PART V. PREPARATION OF BENZYLIDENE AND BENZYL DERIVATIVES OF 4′-ACYL-4-AMINODIPHENYLS

By Vinay S. Misra and Maheswari P. Khare

To investigate the effect of basic strength on antitubercular activity, nine substituted N-benzylidene and the corresponding N-benzyl derivatives of 4′-acyl-4-aminodiphenyls have been prepared.

The well known fact that aromatic compounds have to be highly basic for being antitubercular in nature was first noted by Kuroya (*J. Exper. Med. Japan*, 1929, **7**, 255). A systematic study of such basic compounds, e.g., 4-aminodiphenyl, naphthylamines and aminobenzothiophenes, which were shown to possess high antitubercular activity, was made by several authors (Bloch, Erlenmeyer *et al.*, *Helv. Chim. Acta*, 1945, **28**, 1406 ; 1947, **30**, 1336, 2058, 2063). The other factor which largely contributes to the activity of the synthetic antitubercular compound against *Mycobacterium tubercle* is its high lipoid solubility (Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 2934).

The present work has been undertaken to associate lipoid solubility with varying basicity in the 4-aminodiphenyl moiety, a known antitubercular compound (*loc. cit.*), thus obtaining structures where the antitubercular activity is augmented by these two factors.

The authors have synthesised a series of substituted N-benzyl derivatives of 4′-acyl-4-aminodiphenyls so as to obtain compounds of basic strength, intermediate between those of primary amines and the N-diphenylylamidines, described earlier (Misra and Khare, this *Journal*, 1952, **29**, 695 ; 1953, **30**, 45). The acyl group in the molecule is responsible for the lipophilic nature.

The condensation of 4′-acyl-4-aminodiphenyl with aromatic aldehydes afforded the expected benzylidene derivatives in good yields and these were subsequently catalytically reduced with hydrogen in the presence of platinum black at a pressure of 60 lbs. per. sq. inch to the expected benzylamino compounds. The completion of the hydrogenation was confirmed by testing for the free amino group after boiling with concentrated hydrochloric acid, when it was found to be absent. The fact that complete reduction had taken place was also confirmed by finding out the mixed melting points of the two products.

Experimental

4′-Acyl-4-aminodiphenyl was obtained according to the method described earlier (Misra and Khare, *loc. cit.*).

N-Benzylidene Derivatives of 4′-Acyl-4-aminodiphenyl

These derivatives were obtained in quantitative yields by refluxing equimolar quantities of 4′-acyl-4-aminodiphenyl and freshly distilled aldehydes in alcoholic solution for 30 minutes. The crystalline solid which separated out was filtered after cooling and recrystallised from acetone or dioxane. Their properties are shown in Table I.

TABLE I

Substituted 4′-acyl-4-benzylidene-aminodiphenyls.

[X-$COC_6H_4.C_6H_4N$:CH.C_6H_4-Y]

Substituent. X.	Y.	M.P.	Yield.	Mol. formula	% Nitrogen. Found.	Calc.
CH_3-	H	193-95°	92%	$C_{21}H_{17}ON$	4.81	4.68
CH_3-	*ortho*-OH	197-99°	96	$C_{21}H_{17}O_2N$	4.32	4.44
CH_3-	*para*-OCH_3	218-21°	95	$C_{22}H_{19}O_2N$	4.34	4.25
C_2H_5-	H	177-79°	98	$C_{22}H_{19}ON$	4.63	4.47
C_2H_5-	*ortho*-OH	187-89°	98	$C_{22}H_{19}O_2N$	4.54	4.25
C_2H_5-	*para*-OCH_3	192-94°	96	$C_{23}H_{21}O_2N$	4.48	4.08
C_3H_7-	*ortho*-OH	202°	90	$C_{23}H_{21}O_2N$	3.91	4.08
C_3H_7-	*para*-OCH_3	230-32°	96	$C_{24}H_{23}O_2N$	3.81	3.92
C_3H_7-	*para*-$N(CH_3)_2$	182-84°	86	$C_{25}H_{26}ON_2$	7.08	7.57

N-Benzyl Derivatives of 4′-Acyl-4-aminodiphenyl

The Schiff's bases (0.5 g.), described above, and 30 c.c. of glacial acetic acid were taken in a hydrogenating bottle; 30 mg. of Adams catalyst was added to it and it was shaken in an atmosphere of hydrogen at a pressure of 60 lbs./sq. inch. for 6 hours. The acid was then neutralised with strong ammonia solution and the solid separated was filtered and recrystallised from alcohol or dioxane. Their properties are shown in Table II.

TABLE II

Substituted 4′-acyl-4-benzylaminodiphenyls.

[X-$COC_6H_4.C_6H_4NH.CH_2C_6H_4$-Y]

Substituent. X.	Y.	M.P.	Yield.	Mol. formula.	% Nitrogen. Found.	Calc.
CH_3-	H	148-50°	86%	$C_{21}H_{19}ON$	5.00	4.65
CH_3-	*ortho*-OH	180°	84	$C_{21}H_{19}O_2N$	4.70	4.41
CH_3-	*para*-OCH_3	179-80°	86	$C_{22}H_{21}O_2N$	4.42	4.23
C_2H_5-	H	163-65°	90	$C_{22}H_{21}ON$	4.84	4.44
C_2H_5-	*ortho*-OH	179-82°	87	$C_{22}H_{21}O_2N$	4.62	4.23
C_2H_5-	*para*-OCH_3	182-84°	86	$C_{23}H_{23}O_2N$	4.50	4.06
C_3H_7-	*ortho*-OH	160-61°	80	$C_{23}H_{23}O_2N$	4.12	4.06
C_3H_7-	*para*-OCH_3	163-65°	82	$C_{24}H_{25}O_2N$	4.40	3.90
C_3H_7-	*para*-$N(CH_3)_2$	187-89°	92	$C_{25}H_{28}ON_2$	7.15	7.53

The authors are thankful to Dr. A. B. Sen for his kind interest in the work.

DEPARTMENT OF CHEMISTRY,
LUCKNOW UNIVERSITY,
LUCKNOW.

Received July 11, 1955.

PRESIDENT :

B. C GUHA, D.Sc., PH.D., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

N. R. DHAR, D.Sc., DR.ES.Sc., F.R.I.C., F.N.I.
B. B. DEV, D.Sc., F.R.I.C., F.N.I.
SIR J. C. GHOSH, KT., D.Sc., F.N.I.
P C. GUHA, D.Sc., F.N.I.
J. N. MUKHERJEE, C.B E., D.Sc., F.A.S.B., F.N.I.
MATA PRASAD, D.Sc., F.R.I.C., F.N.I.
J. N. RAY, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. RÂY, M.A., F.N.I.
B. K. SINGH, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

U. P. BASU, D.Sc., F.N.I.
B. SANJIVA RAO, D.Sc., PH.D., F.N.I.
K. VENKATARAMAN, D.Sc., PH.D., F.R.I.C., F.N.I.
D. B. LIMAYE, M.Sc.,
President of Poona Branch (*ex-officio*)

HONY. SECRETARY :

S. K. MUKHERJEE, D.Sc.

HONY. TREASURER :

B. N. GHOSH, D.Sc., F.N.I.

MEMRERS OF THE COUNCIL :

D. K. BANERJEE, D Sc.
P. K BOSE, D Sc , F.N.I
D. CHAKRAVARTI, D Sc., F.N.I.
MRS. ASHIMA CHATTERJEE, D Sc.
B. CHATTERJEE, D.Sc.
A. C. CHATTERJI, D.Sc., DR. ING., F.N.I.
H. N. DAS GUPTA, D Sc.
R. D. DESAI, D.Sc., F.R.I.C., F.N.I.
S. S. JOSHI, D.Sc., F.R.I.C., F.N.I.
M. N. GOSWAMI, M.A., DR.EN.CH.
T. N. GHOSH, D.Sc., F.N.I.
J. GUPTA, D.Sc.
A N KAPPANNA, D Sc , F.N.I.
R. P. MITRA, D.Sc., F.N.I.
S. M. MUKHERJI, D.Sc., Ph.D.
P. V. NAIR, M.Sc., D.PHIL.
A. B. SEN, M Sc., PH.D.
V. SUBRAHMANYAN, D.Sc., F.R.I.C , F.N.I.
S. H. ZAHEER. M.A., PH.D.

HONY. EDITORS :

S. R. PALIT, D.Sc., F.R.I.C., F.N.I.
R. C. SHAH, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

D. K. BANERJEE, D.Sc.
P. K. BOSE, D.Sc., F.N.I.
B. CHATTERJEE, D.Sc.
J. K. CHOWDHURY, M.Sc., PH.D., F.N.I.
P. C. DUTTA, D.Sc.
B. N. GHOSH, D Sc., F.N.I.
J. C. GHOSH, D.Sc., F.N.I.
A. N. KAPPANNA, D.Sc., F.N.I.
S. K. MUKHERJEE, D.Sc.
B. C. GUHA, D.Sc , PH.D., F.N.I.
P. RAY. M.A., F.N.I.
T. R. SESHADRI, M.A., PH.D., F.N.I.
P. B. SARKAR, DR.ES. Sc., F.N.I.
K. VENKATARAMAN, D.Sc., PH.D., F N I

HONY. AUDITORS :

P. C. NANDI, M.A., B.Sc., A.C.A.R.A.
A. B. GUPTA, B.Sc., L.L.B.,A.C.A.R.A.

ASST. SECRETARY:
B. C. ROY, M.Sc.

ASST. EDITOR :
G. BANERJEE, M.Sc.

Let us assist you in furnishing Your Research Laboratory with most up-to-date dependable apparatus manufactured by us.

The Luxmi Scientific Glass Works

4/8, Ultadanga Main Road, Calcutta-4.

UNIQUE IN INDIA

An offer to Scientists & Research Institutes

ELCO TRADE MARK PRODUCTS

We Manufacture :—

1. MICROSCOPIC SLIDE CABINETS
   To hold 2000 slides in horizontal position (Flat) in 100 Aluminium trays in a very dainty looking cabinet with locking arrangement.
2. MICROSCOPIC SLIDE CABINETS & BOXES
   of various Sizes & Capacity for SLIDE in vertical position.

OUR OTHER PRODUCTS :—

Burette and Funnel stands of improved design, Test tube & Reagent bottle stands etc.

Price-list on request.
Agents required for every Province
Apply

LILA & COMPANY

POST BOX NO. 7848 : : CALCUTTA-12, INDIA

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

ask

MANSFIELD'S

for

SPECIALISED TESTING INSTRUMENTS

for

The Chemical, Paint, Rubber, Sugar Oil, Cement, Metals & Mining Industries
Meteorological & Surveying Instruments
Laboratory Glassware & Apparatus

* * *

MANSFIELD OIL GAS CO.; LTD.

P.O. Box 124, Calcutta-15

Branches : **Madras 1.**

Naogoaon & Rajshahi (E. Pakistan)

For Laboratory *Reagent Quaility* Acids

To Precise Specifications

Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4: 98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3: 69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl: 35.39% w/w Sp. gr. 1.8 at 15°.
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements
for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

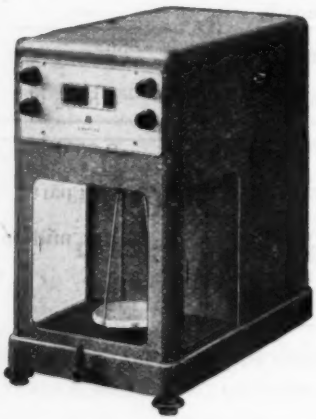
Office : 94, Chittaranjan Avenue, Calcutta-12

HELVETICA CHIMICA ACTA

The HELVETICA CHIMICA ACTA, founded in 1918, publishes in one of the three national languages the principal results of research work in pure chemistry carried out in Switzerland. The HELVETICA CHIMICA ACTA are property of the Swiss Chemical Society. Annually 7-8 numbers are published which members receive without charge.

All correspondence concerning membership of the Swiss Chemical Society or subscriptions for the HELVETICA CHIMICA ACTA should be addressed to :

SWISS CHEMICAL SOCIETY, BASLE 7.



The competent chemist always prefers the

METTLER-ANALYTICAL BALANCE

MADE IN SWITZERLAND

With the following advantages :—

-Automatic operation of the weights up to 200 Grams.

-Large optical scale of 115 Mgs.

-Constant loading of the beam giving highest precision throughout the complete range.

-Reading of the weights on one single scale.

Sole Agents :—

RAJ-DER-KAR & Co.

COMMISSARIAT BUILDING

HORNBY ROAD,

FORT BOMBAY.

Telephone. 27304. Telegram : 'Techlab'

Weight = 123.7306 grams.

-EXACT-QUICK-SURE-SIMPLE.

-Service facilities available at BOMBAY, MADRAS & CALCUTTA.

Ask for offers and detail literature.

Phone—34-3176. Telegrams—Nadiachemi.

NADIA CHEMICAL WORKS LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :—

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

Large Stockists of:

Quickfit Interchangeable Standard Joints and Assemblies etc.

and

Manufacturers of any kind of special Glass Apparatus of soft or Pyrex Glass.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : B. B 4911. Gram : Siganiko.

Gram : "Presglako."

PREMIER SCIENTIFIC G. CO.

26/2A, Prosonna Kumar Tagore Street, CALCUTTA-6

Stockist for

E. MERCK, DARMSTADT

CHEMICALS. STAINS, INDICATORS, ACIDS, ETC.

Also

APPARATUS, CHEMICALS, GLASS WARES, FILTER PAPERS, MICROSCOPES ETC.

For

SCHOOLS, COLLEGES, ANALYTICAL & RESEARCH LABORATORIES AND DOCTORS.

INDEX + SIGCOL +

DO YOU KNOW

Sigcol **Index** combines **three** in **one** ? Behind every **Index** beaker and flask you can see long experience backed by scientific research. **Index** is a symbol of gurantee for laboratory work It i

* Resistant to Chemical reagents
Resistant to mechanical shocks
* Resistant to heat (coefficient of expansion is only 3.4×10^{-6}).

Sole Distributors :

GHARPURE & CO

P-36, Royal Exchange Place Extn.

Calcutta 1

FOR RAPID & ACCURATE CHEMICAL ANALYSIS

USE

TINSLEY POLAROGRAPH

WITH DERIVATIVE CIRCUT

Here are some advantages:

* MICRO ANALYSIS
* HIGH SENSITIVITY
* QUALITATIVE AND QUANTITATIVE ESTIMATION
* SIMULTANEOUS ESTIMATION OF SEVERAL CONSTITUENTS ON ONE POLAROGRAM
* ADAPTABILITY: ANALYSIS OF METALS, ORGANIC & INORGANIC SUBSTANCES ON THE SAME SAMPLE
* REPEATED ANALYSIS
* SIMPLIFIED OPERATION FOR USE BY SEMI-SKILLED STAFF
* ROUTINE ANALYSIS WITH SPEED AND ACCURACY.

For Further particulars, please contact

Sole Agents in India:

PIONEER INDUSTRIES

20, British Indian Street, CALCUTTA-1. | 21, Forbes Street, BOMBAY-1. | 193, Mount Road, MADRAS-2.

We Manufacture

POTASSIUM DICHROMATE

(Analytical Reagent)

MAX. LIMIT OF IMPURITIES

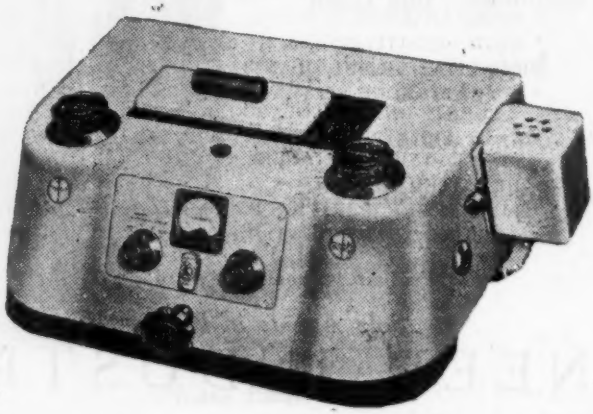
CHLORIDE	...	...	...	0.0005%
SULPHATE	...	...	...	0.01%
CALCIUM	...	...	...	0.005%

Tested by the Govt. Test House, Alipore

THE INTERNATIONAL CHEMICAL INDUSTRIES

103-B, Upper Circular Road, Calcutta-9

DETERMINATION OF POTASSIUM IN WATERS & SERUM



UNICAM SP-600 SPECTROPHOTOMETER

The application of Unicam SP-600 Spectrophotometer in the determination of Potassium in waters and Serum has been worked out in the laboratories of Harry Pritchard, M.Sc., F.R.I.C. The method employed for the said specific purpose (with suitable modifications) will enable the SP-600 to be used for the determination of Potassium in a wide variety of materials.

SOLE AGENT

THE SCIENTIFIC INSTRUMENT COMPANY LTD.

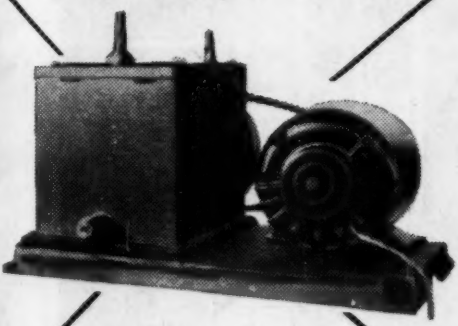
CALCUTTA, ALLAHABAD, NEW DELHI, MADRAS, BOMBAY.

MADE IN INDIA

HIGH VACUUM ROTARY PUMP

Single Stage & Two Stage

Suitable for Laboratory use and similar in performance to those made in Germany, England & U. S. A.



All Indian Materials and Constructions.

BASIC & SYNTHETIC CHEMICALS LIMITED
P. O. Jadavpur College, Calcutta-32

VERY RELIABLE INDIGENOUS SUBSTITUTES OF GUARANTEED ANALYTICAL REAGENTS MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

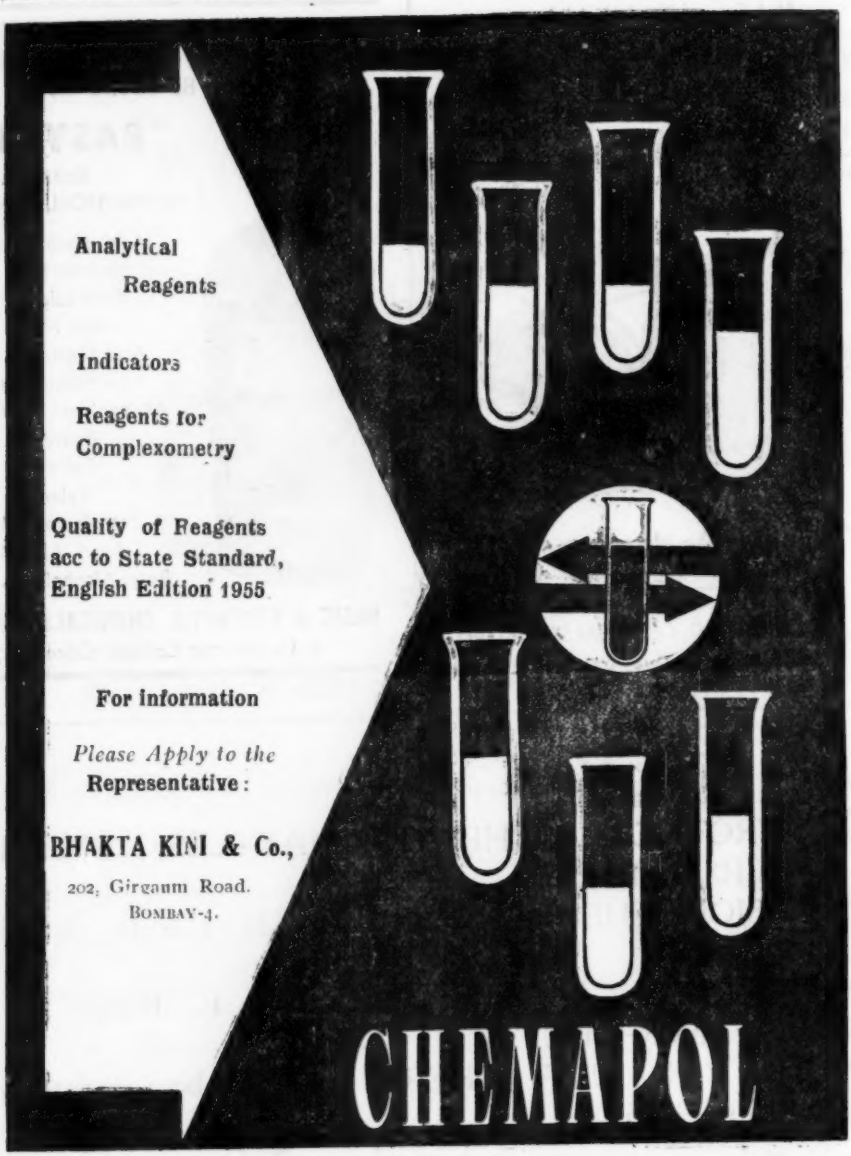
Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

BASIC & SYNTHETIC CHEMICALS LIMITED
P. O. Jadavpur College, Calcutta-32

We offer:

* METTLER Balances.
* ELECTROTHERMAL HEATING MANTLES, ARMOURED HEATERS & TAPES.
* PRECISION THERMOSTATIC BATH I & E, Sensitivity 0.01°C.
* OVENS HIGH TEMPERATURE I & E, Range 50° to 300°C, Sensitivity ± 1°C.
* INCUBATOR MULTI - THERM I & E, 5° above room temperature to 200°C ± 0.5°C.

INSTRUMENTS & EQUIPMENTS
35, CHITTARANJAN AVENUE,
CALCUTTA-12



PRAHA, CZECHOSLOVAKIA

SERVING for LAST 38 YEARS

LABORATORY CHEMICALS & REAGENTS :

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

Acetone
Acid Acetic glacial 99-100%
Alcohol Amyl
Alcohol Methyl
Barium Carbonate
Barium Chloride
Benedicts' Solution
Benzene
Carbon Tetrachloride
Lead Acetate
Liquor Ammon Fort (24/27%)
Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, Panditia Road, Calcutta 29.
BRANCH OFFICES : Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.

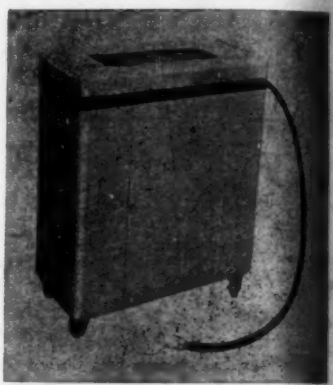
Regtd. No. C1878

MULLARD

ULTRASONIC GENERATOR

E. 7562

This equipment is a general purpose high ultrasonic frequency generator for use in research or for incorporation into industrial plant, and it is capable of providing the highest ultrasonic power outputs that are at present within the reach of commercial equipment. Set covers the frequency range, up to 2 Mc/s, in which high intensities can be generated by a reasonably robust quartz crystal. The associated crystal holder has been specially designed for immersion in a conducting liquid, thus avoiding the inconvenience and power loss associated with the normal practice of operating crystals under oil. Holders can be provided building into tanks for clearing and other applications.



Design Features:

* Covers frequency range 250-2000 kc/s.
* Electrical outputs up to 600 W at 2Mc/s.
* Designed for extreme simplicity of control.
* Self-contained in wheeled cabinet for transportable use.

Also Available

Conductivity Meter ; Conductivity Controller ; Temperature Controller ; Potentiometric Titration Apparatus; Ultrasonic Soldering Iron, Ultrasonic Cleaning Baths, etc.

SOLE AGENTS IN INDIA

TOSHNIWAL BROTHERS LTD.

198, Jamshedji Tata Road, BOMBAY 1.

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunj, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.

use in
ighest

metric

D.

gang.